

Investigations on Al₂O₃-C Refractories with a Self-glazing Effect

V. Roungos, C.G. Aneziris

Al₂O₃-C refractories are widely used as functional refractory components in steel applications. Due to their poor oxidation resistance, these components are coated with a protective glaze to inhibit carbon oxidation. An innovative improvement is the development of glaze-free refractories. The present article describes investigations concerning the production of self-glazing Al₂O₃-C refractories. Various heat treatments in air atmosphere have been examined for their suitability to produce the self-glazing effect. The phase composition and microstructure of the specimens was studied using X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS), while the physical properties were determined by means of Hg-porosimetry measurements. The results showed that a self-glazing surface could be achieved via special heat treatment. The critical temperature range affecting the glaze formation was 600 – 1300 °C. The rather dense self-glaze was a few hundred microns thick and adhered well to the carbon-bonded refractory substrate. However, some pinholes were also present in the glaze structure. Further investigations are required in order to optimize the control of self-glaze formation. In addition, the corrosion and thermo-mechanical behaviour of self-glazing Al₂O₃-C refractories needs to be evaluated in order to determine the application potential of these refractories for steel casting equipment.

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1 Introduction

Al₂O₃-C refractories are widely used as functional refractory components in steel applications (monobloc stoppers, submerged entry nozzles). The combination of alumina with graphite gives these refractories outstanding behaviour in terms of resistance to thermal shock, corrosion, erosion and spalling, as well as high mechanical strength and low wettability by slags and molten steel. The main drawback of the material is its poor oxidation resistance, due to the carbon content. The measures taken against carbon oxidation include the use of antioxidants, in most cases metallic Si and Al fine

Tab. 1 Investigated Al₂O₃-C composition

Raw materials	Composition [mass-%]
Al ₂ O ₃	59
Graphite	25
Novolac resin	6
Hardener	0,6
Si	4
SiO ₂	4
Na ₂ B ₄ O ₇	2

powders [1–6], and protective glazes applied to the outside surfaces of the components [7, 8]. The metallic additions also contribute to the reinforcement of the refractories due to the formation of metal carbides and/or nitrides [1–6]. Moreover, the external glaze further increases their mechanical strength.

A challenge that could open entirely new potentials for the application of carbon-bonded refractories is the development of glaze free Al₂O₃-C refractories with a self-glazing surface achieved by heat treatment in air atmosphere. Self-glazing effects have been known in the ceramic industry for over a century, especially in sanitary ceramics, tiles and flatware porcelain [9]. Refractory crucibles on SiC basis with self-glazing effects are also known, however these products are additionally coated externally with flux materials [10].

2 Experimental

Commercial grades of alumina and graphite were used for the production of the Al₂O₃-C samples. The alumina grades used were a fused alumina fine grade (99,70 mass-% Al₂O₃, 0,16 mass-% Na₂O) and a tabular alumina coarse grade (99,50 mass-% Al₂O₃, max. 0,40 mass-% Na₂O). The maximum grain size of the alumina grades was 0,60 mm. The natural graphite grades used were

a very fine ground natural graphite (96 – 97 mass-% carbon content) with 99,5 mass-% less than 40 µm, and a normal flake graphite (94 – 96 mass-% carbon content) with 95,0 mass-% < 71 µm. The binder used in all compositions was a novolac type phenolic resin. Hexamethylene tetramine was used as hardener. All additives had high purity and 99,5 mass-% of the grains were < 200 µm. The additives used in the investigated composition (Tab. 1) were metallic Si, SiO₂ and Na₂B₄O₇ (borax).

All the raw materials and additives were mixed at room temperature following the standard commercial practice. After mixing, cylindrically shaped specimens (diameter 50 mm, height 45 mm) and bar-shaped specimens (25 mm x 25 mm x 150 mm) were uniaxially pressed at 100 MPa. The pressed specimens were cured at 180 °C and finally coked in a retort filled with coke breeze. The coking temperature was 1400 °C and the soaking time was 5 h.

Oxidation tests were carried out for the initial evaluation of the self-glaze formation. The cylindrically shaped specimens were placed in a specially equipped furnace, with their weight being registered during the oxidation tests. The tests were carried out at 1450 °C in air atmosphere, using various heating rates and a soaking time of 5 h. The phase composition and microstructure after the oxidation tests were evaluated with the aid of X-ray diffraction (XRD), optical microscopy, scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS). Finally, the physical properties of the specimens were determined with a Hg-porosimeter (Pascal 140/440, Thermo Electron Corporation).

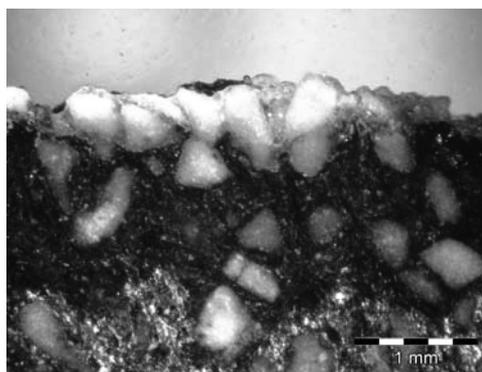


Fig. 3 Cross section of a typical area of the self-glaze

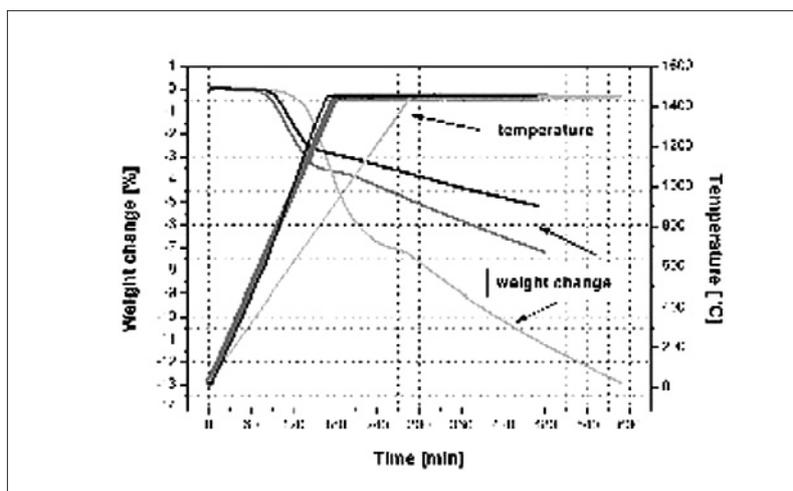


Fig. 1 Weight loss of the samples at different heating rates

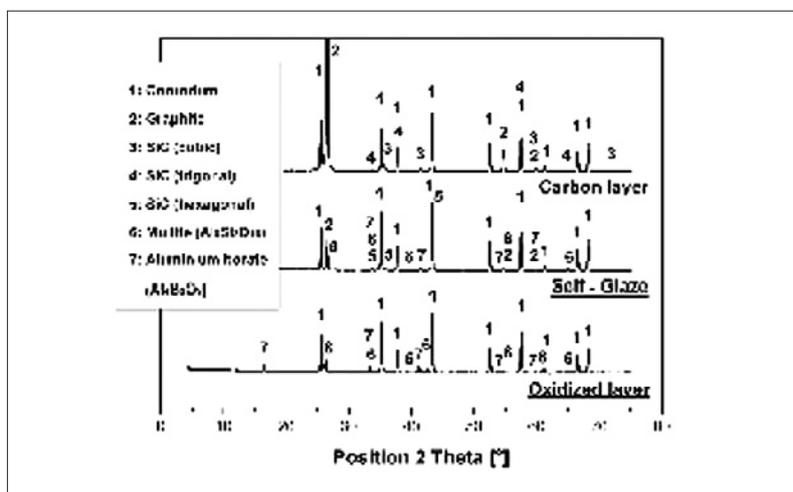


Fig. 2 Identified phases after the oxidation resistance tests

3 Results and discussion

The weight loss of the specimens, expressed in %, has been used for evaluating their oxidation resistance. Fig. 1 shows the oxidation resistance of the cylindrical-shaped samples as a function of heat treatment. The weight change of the specimens (left y-axis) and the temperature (right y-axis) are correlated as a function of time. Each temperature curve has the same colour as the related weight change curve. The testing temperature of 1450 °C and the soaking time of 5 h were constant for all oxidation resistance tests.

The sample subjected to a heating rate of 5 K/min (light grey) had a weight loss of 12,9 %, while the specimens treated with a heating rate of 8 K/min (dark grey) exhibited a weight loss of 7,2 %. A third specimen was heated to 600 °C at a rate of 8 K/min

and to 1300 °C at the maximum allowable heating rate of 10 K/min, followed by heating to 1450 °C at a rate of 8,3 K/min. This specimen exhibited the best oxidation resistance, having a weight loss of only 5,1 %. The reason for the choice of the third specimen's heat treatment is pretty obvious observing the curves in Fig. 1. It can clearly be 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 specimens is proceeding, with the oxidation rate highly dependent on the extent of self-glaze formation on the outer surface of the specimens.

The phase compositions of the samples after the oxidation resistance tests were deter-

mined by X-ray diffraction (XRD). The investigated samples were taken from all three layers, i.e. the carbon layer, the oxidized layer and the self-glaze layer (Fig. 2). The identified phases in the carbon layer were corundum, graphite and two modifications of SiC, a cubic and a trigonal one. As expected, no free Si could be detected. Besides corundum, mullite and an aluminium borate phase were identified in the sample of the oxidized layer. The absence of SiO₂ phase can be pointed out here. These three phases were identified in the sample of the self-glaze as well, together with graphite and a third, hexagonal modification of SiC. The presence of graphite and SiC in the self-glaze sample is not only an evidence of its high adhesion to the carbon layer, but also an indication of the bonding between the self-glaze and the carbon-bonded refractory substrate.

The self-glaze microstructure was investigated via optical microscopy and scanning electron microscopy/energy dispersive X-ray spectroscopy (SEM/EDS). Following the standard specimen preparation methodology, the sample was firstly embedded in an epoxy resin. Metallographic specimen preparation was performed perpendicular to the outer surface up to 1 µm grain size. Then, the specimen was vibratory polished for 1 h (Buehler VibroMet 2) with a grain size of 0,02 µm. Finally, the specimen was coated with Pt for 10 s for the SEM investigations.

A typical optical microscopy image of the specimen is shown in Fig. 3. The self-glaze on the outer surface can be clearly seen and it can be concluded that it is rather dense. This is verified by the SEM micrograph of the self-glaze, shown in Fig. 4.

The phases present were identified with the aid of elemental analysis via energy dispersive X-ray spectroscopy. The results are shown in Fig. 5. The elemental analysis was carried out in the self-glaze area, which was of main interest. The SEM micrograph of the self-glaze area in cross section is shown in the upper left field of Fig. 5, and the associated distribution of the elements of interest is shown in the upper right (for carbon) and the lower fields (for silicon, oxygen and aluminium) of Fig. 5. Unfortunately, the element boron which was also of interest could not be detected with the available EDS device.

The outer surface area of the specimen, i.e. the self-glaze area, is rather dense and obvi-

ously has corundum as its major component. Furthermore, it has a thickness of a few hundred micrometres (around 200 – 400 µm). The elemental analysis of silicon shows enrichment along corundum grain boundaries, which is an evidence of mullite crystal formation (in areas where silicon, oxygen and aluminium coexist). The silicon concentration decreases from the self-glaze surface to the inner carbon-bonded refractory. Areas where silicon and carbon coexist, which would indicate the formation of a SiC phase as identified via XRD analysis, were not readily found. This can be explained from the relatively large area shown in Fig. 5 in combination with the in-situ formation of various SiC structures, all of which have extremely small grain sizes (either plate-like crystals or fibres and whiskers) as shown in Figs. 6 and 7.

As for the elemental analysis of carbon, two concentrations can be detected. The first one is at the right side of the specimen and is caused by the epoxy resin from the specimen preparation. The second is distributed in the

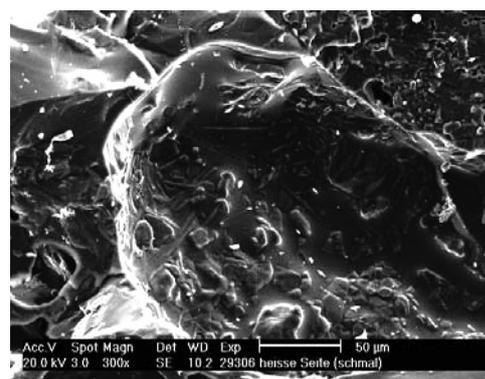


Fig. 4 SEM micrograph of the self-glaze

interface between the self-glaze and the inner refractory body and concerns the glass-like carbon binder of the Al₂O₃-C refractory. As already mentioned, the physical properties of the specimens were determined with a Hg-porosimeter. These investigations included specimens from all three layers, i.e. the carbon layer, the oxidized layer and the self-glaze area, of the refractory after the oxidation resistance test. The results of open porosity versus pore size distribution are

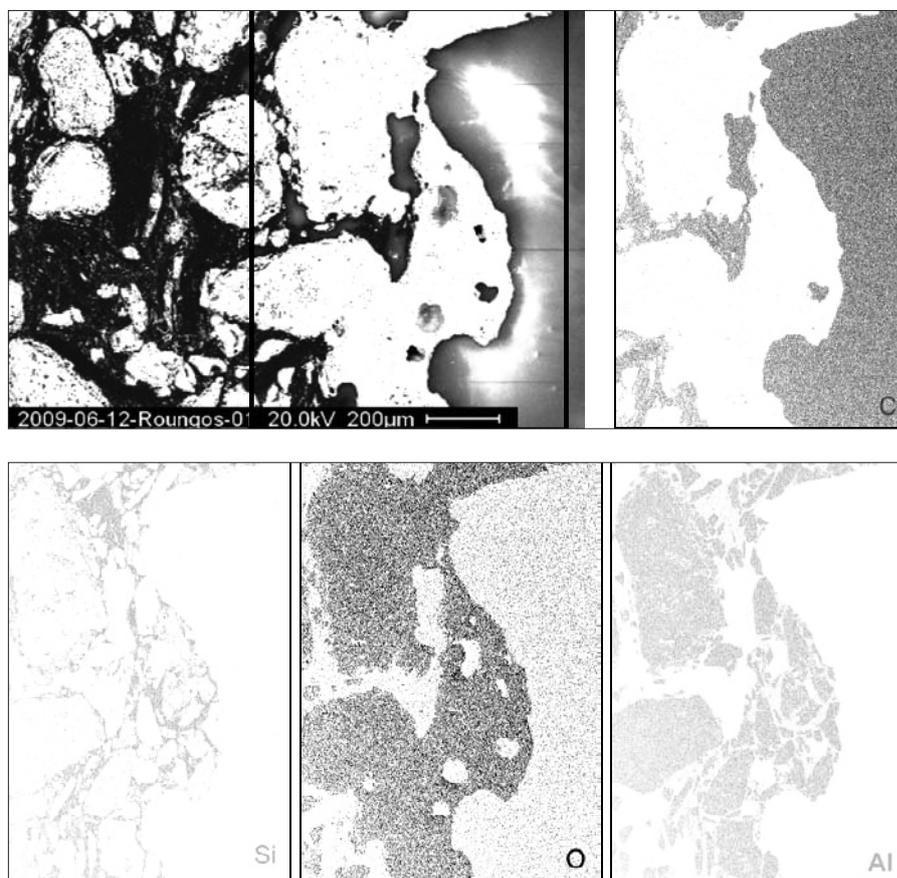


Fig. 5 SEM micrograph of the self-glaze area in cross section and associated distribution of the elements C, Si, O and Al

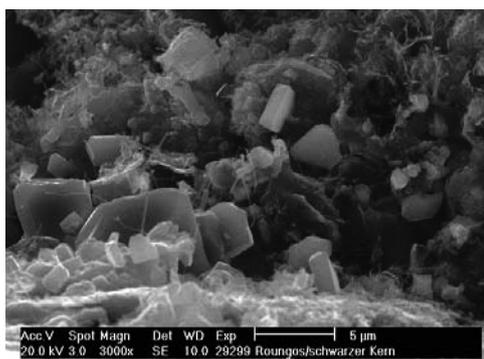


Fig. 6 SEM micrograph cubic and trigonal SiC structures formed in situ

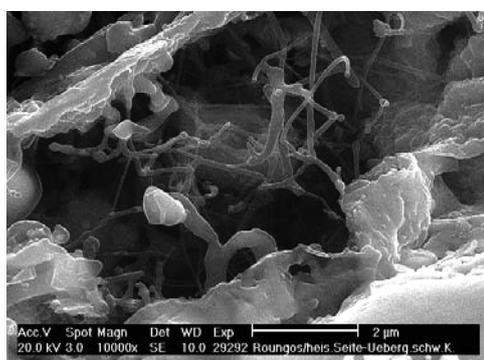


Fig. 7 SEM micrograph of SiC fibres and whiskers formed in situ

shown in Fig. 8. Open porosity was highest in the carbon layer specimen (20,8 %), followed by the self-glaze and the specimen from the oxidized layer (19,3 % and 18,4 % respectively). To avoid misleading conclusions, it has to be pointed out here that the results of the porous structure of the self-glaze specimen are strongly influenced by the porous structure of the carbon layer, since it was not possible to completely separate these two layers. Based on the oxidation resistance results, it was able to achieve complete and homogeneous self-glaze formation on specimens which were heat treated at 21 K/min up to 1300 °C, followed by soaking for 5 h (Fig. 9). The open porosity in the self-glazed specimens determined using Archimedes' principle was around 10 % and mostly concerned glaze defects such as pin-holes. As for the porous structure of the oxidized specimen, it can be regarded as the worst one, despite its lower open porosity compared to the specimen from the carbon layer. The reason is simply because the oxidized layer had much greater pore sizes (the median pore diameter was 105 µm) compared with the specimen from the carbon

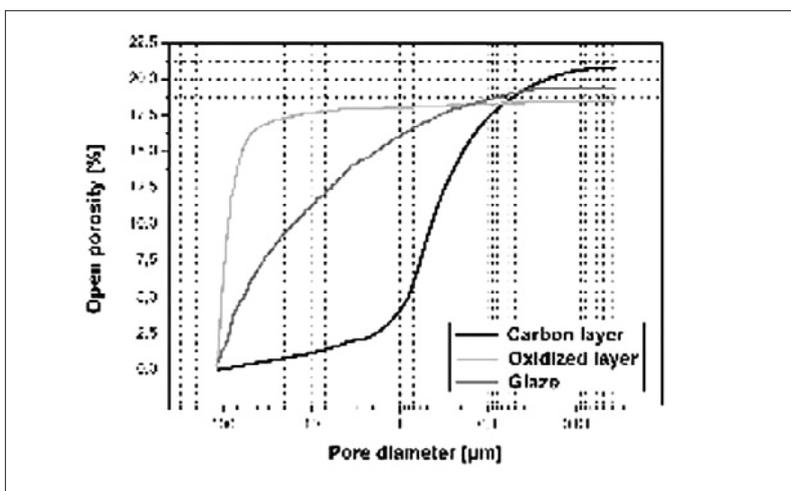


Fig. 8 Porous structure of various layers of the investigated Al₂O₃-C refractory after oxidation resistance test

layer, which had a median pore diameter of 0,47 µm. Thus, no oxidation suppression can be achieved in areas where the self-glazing effect is not present. It is assumed that the overall lower open porosity of the oxidized layer is very likely due to the start of sintering (after a soaking time of 5 h at 1450 °C). This assumption is supported by the results of bulk density measurements, which were 2,44 g/cm³ for the carbon layer and 2,64 g/cm³, i.e. slightly higher, for the oxidized layer. Porous structure measurements of self-glazed specimens, with the side of the carbon layer sealed (e.g. with epoxy resin), will be presented in a future work.

4 Conclusions

In the present work the phase composition, the microstructure and the physical properties of Al₂O₃-C refractories with a self-glazing surface were studied when subjected to air at high temperatures. Oxidation resist-

ance tests showed a clear correlation between the heating rate and the effectiveness of self-glaze formation on the outer surface of the refractory. The critical temperature range affecting glaze formation was 600 – 1300 °C. Based on these results, it was possible to achieve complete and homogeneous self-glaze formation on the outer surface of the samples in conjunction with a special heat treatment process. The results of this study will be presented in detail in a future work.

Interesting information was also gained from the phase composition investigations, which showed that no free SiO₂ phase was present, because it had all reacted either to mullite or to aluminium boron silicate glass (self-glaze). Moreover, the in-situ formation of various modifications of SiC phase (polytypes) gives an indication of the complexity of the system from a kinetic point of view. It is believed that the various SiC structures are

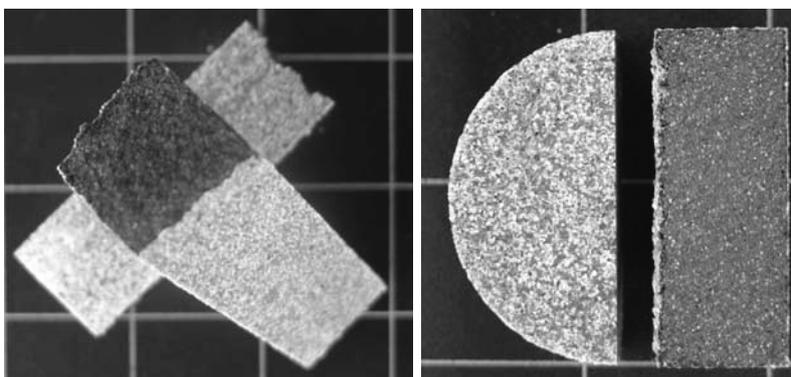


Fig. 9 Complete and homogeneous self-glaze formation on Al₂O₃-C refractories after special heat treatment, a) bar-shaped sample, b) cylindrically shaped sample

advantageous not only for the thermo-mechanical behaviour of the refractory but also for the bonding of the self-glaze layer and its adhesion to the carbon-bonded refractory substrate.

Nevertheless, some pinholes were also present in the glaze structure. Further investigations have to be carried out in order to optimize the control of self-glaze formation. In addition, the corrosion and thermo-mechanical behaviour of self-glazing $\text{Al}_2\text{O}_3\text{-C}$ refractories needs to be evaluated in order to determine the application potential of these refractories for steel casting equipment.

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