The Effect of Zirconium Disilicide (ZrSi₂) Additions on the Carbon Oxidation Behavior of Alumina/Graphite Refractory Materials

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Carbon oxidation is a main industrial problem for Alumina/Graphite Submerged Entry Nozzles (SEN) during pre-heating. Thus, the effect of ZrSi₂ antioxidants and the coexistence of antioxidant additive and (4B₂O₃·BaO) glass powder on carbon oxidation were investigated at simulated non-isothermal heating conditions in a controlled atmosphere. Also, the effect of ZrSi₂ antioxidants on carbon oxidation was investigated at isothermal temperatures at 1473 K and 1773 K. The specimens’ weight loss and temperature were plotted versus time and compared to each others. The thickness of the oxide areas were measured and examined using XRD, FEG-SEM and EDS. The coexistence of 8 wt% ZrSi₂ and 15 wt% (4B₂O₃·BaO) glass powder of the total alumina/graphite base refractory materials, presented the most effective resistance to carbon oxidation. The 121% volume expansion due to the Zircon formation during heating and filling up the open pores by (4B₂O₃·BaO) glaze during green body sintering led to an excellent carbon oxidation resistance.

KEY WORDS: refractory; ZrSi₂; graphite; alumina; oxidation.

1. Introduction

The steel industry consumes almost 50% of the total produced refractory materials in the world and a large proportion of this consumption is graphite containing refractories.¹ Here, the Submerged Entry Nozzle (SEN) used during continuous casting is almost just made of alumina/graphite refractory. The presence of graphite in the SEN base refractory materials leads to¹):

• A high thermal shock resistance and a high thermal conductivity which make it possible to pre-heat the SEN at higher heating rates. This, in turn, leads to saving time and energy.
• A low wettability by molten steel.

Graphite in the SEN base refractory materials may be oxidized directly in an oxidizing atmosphere such as in an oxygen- or a carbon dioxide-rich atmosphere. Furthermore, by indirect oxidation as reaction (1) presents. More specifically, graphite oxidation starts at 873–973 K in air to form carbon monoxide or carbon dioxide.²¹

\[ C(s) + \text{SiO}_2(\text{O}) = \text{CO}(\text{g}) + \text{SiO}(\text{g}) \quad \text{(1)} \]

A method to inhibit the decarburization of AlₓOᵧ–C refractories is the addition of so-called antioxidants. An antioxidant is an element or a compound with a high oxidation affinity. Aluminum is the most conventional antioxidant, but the formation of AlₓCᵧ after sintering of the green body may be a disadvantage. This is due to that the AlₓCᵧ compound may be hydrated even at room temperature to form an Al(OH)₃ compound as reactions (2) and (3) suggest. This, in turn, may lead to volume expansion and cracking of the refractory bulk.³¹

\[ 4\text{Al}(l) + 3\text{C}(s) = \text{Al}_4\text{C}_3(s) \quad \text{.........(2)} \]

\[ \text{Al}_4\text{C}_3(s) + 12\text{H}_2\text{O}(\text{g}) = 3\text{CH}_4(\text{g}) + 4\text{Al(OH)}_3(s) \quad \text{.........(3)} \]

Sunayama et al.⁴ have investigated the influence of aluminum additions on the oxidation rate of Magnesia/graphite refractory, which showed a slight improvement of the oxidation resistance at temperatures below 1823 K. Wang et al.⁵ have investigated the influence of AlₓBᵧCᵧ additions on the decarburization resistance of magnesia/graphite refractory. In addition, Gokce et al.⁶ have evaluated the effects of various antioxidants such as Si, Al, BₓC and SiC on the decarburization resistance of magnesia/graphite refractory. Overall, only a few researchers such as Youqi et al.⁶ and Dejiang et al.⁷ have investigated the effects of antioxidants on the decarburization resistance of alumina/graphite-based refractory materials. More specifically, Youqi et al.⁶ investigated the effect of a metallic Zn addition on the carbon oxidation and established the severe Zn volatilization during green body sintering. Dejiang et al.⁷ established the remarkable carbon oxidation resistance of the refractory due to the silicon-containing boron glass coating. Furthermore, Wang and Yamaguchi⁸ have also reported the coexistence effects of liquid phase and the additives oxidation products to inhibit the oxygen penetration. They reported the positive effects of liquid diboron trioxide on the decarburization resistance. On the other hand, Peng et al.⁹ have found a severe volatilization of B₂O₃ at temper-
Table 1. Relative volume increase during oxidation of aluminum and other intermetallic compounds.9)

| Reaction                  | Relative Volume Expansion [Volume percent] |
|---------------------------|-------------------------------------------|
| 2 Al + 3/2 O₂ → Al₂O₃     | 29                                        |
| ZrSi₂ + 3 O₂ → ZrSiO₃ + ZrO₂ | 71                                        |
| ZrSi₂ + 3 O₂ → ZrSiO₃ + SiO₂ | 121                                       |

2.2. Samples Preparation and Examination

60 wt% alumina, 10 wt% silica and 30 wt% flake graphite powders were mixed in a ball mill using corundum balls for 24 h to prepare the Refractory Base Material (RBM). Different samples were prepared by addition of different amounts of ZrSi₂ and (4B₂O₃·BaO) glass powder into the RBM, as Table 2 shows. Poly Vinyl alcohol (PVA) which is a conventional organic binder in alumina mixtures was used as binder.11) More specifically, about 30 vol% of the mixture was finally added as a binder material. Each Powder mixture was then grinded for 24 h in a corundum ball mill.

The powder mixture was uniaxially pressed at 215 MPa to form a cylinder with a 17 mm diameter and about 17 mm height. Then, the green body was embedded by active graphite powder in a graphite crucible. Thereafter, the graphite crucible was heated to 513 K in an electrical box furnace in air for 5 h to obtain a degradation of PVA. Finally, the crucible was heated at 9 K/min to 1373 K in a high-temperature graphite resistance furnace for 8 h in an argon atmosphere, at a flow rate of 3 NL/min.

All samples observations and chemical compositions were determined using an Ultra 55 Field Emission Gun Scanning Electron Microscope so called FESEM (Carl Zeiss equipped by EDS Inca Penta FETX3 Oxford Instrument). Also, the thickness of the decarburized layer was measured using a calibrated Olympus SZX16 light optic microscopy equipped by a 3CCD Color Version Camera Module and Image-Pro Plus software with measurement accuracy of ±10 μm.

2.3. Experimental Apparatus

Figure 2 shows the experimental apparatus to perform the carbon oxidation experiments. The sample was suspended by a platinum wire inside the alumina tube of the electrical furnace. Here, the sample weight was measured with a thermobalance with an accuracy of ±0.01 g. The thermobalance was connected to a computer equipped with a Balance-Win software (version 3.0.13), which gathered the real time sample weight every second. The Pt-10%Rh/Pt thermocouple showed the real time temperature.

2. Experimental Procedure

2.1. Raw Materials

The raw materials used in this work were crystalline flake graphite (99.9% purity, ≤5 μm), tabular corundum (99.4% Al₂O₃ and 0.12% Fe₂O₃, ≤300 μm), Silica (99.9% purity, ≤45 μm), diboron trioxide (99.98% purity, ≤45 μm), barium oxide (99.5% purity, ≤45 μm) and zirconium disilicide (99.5% purity, ≤45 μm). To produce the (4B₂O₃·BaO) glass powder, 64 wt% B₂O₃ and 36 wt% BaO powders were weighted using a balance at ±1 mg weight accuracy. Thereafter, powders were mixed and grinded in a ball mill grinding 24 h. The mixture was uniaxially pressed at 100 MPa. In addition, the green body was heated in a graphite crucible to 1223 K and at a rate of 9 K/min. This was done for 1 h using argon at a flow rate of 3 NL/min, as an inert atmosphere. The formed glaze was first crushed in a mortal to powder. Thereafter, milled in a ball mill grinding operation for 48 h by using corundum balls.
near the suspended sample with an accuracy of ± 1 K.

It should be noticed that the carbon oxidation resistance evaluation of the antioxidant containing alumina/graphite used in Submerged Entry Nozzle (SEN) base refractory material, during pre-heating was the most important aspect of this work. Therefore, the temperature profile which the samples were supposed to follow during heating had to be similar to that found in industrial conditions. A commercial alumina/graphite refractory pre-heating simulation performed from 373 to 1 773 K to suggest the temperature profile for the laboratory trials.

2.4. Pre-heating Simulation

The temperature profile for heating of samples has been decided by the commercial Submerged Entry Nozzle (SEN) pre-heating simulation using COMSOL Multiphysics® software (version 3.5). It assumed that inside diameter of the SEN is constant at 0.036 m and its shape is symmetrical so that simulation can be performed in 2D. The selected commercial SEN, alumina/graphite refractory, had a heat conduction coefficient of 18 (W/m · K) at 973 K, a density of 2430 (kg/m 3) and a specific heat capacity of 1 416.56 (J/kg · K). The heating source is assumed to be a propane combustion torch with a fuel consumption of about 10 kg/h. The propane flue gas volume for combustion was assumed to be 13.11 (Nm3/kg Propane) with a temperature of 1 773 K. The propane flue gas velocity is calculated as 35 m/s using Eq. (4), while the nozzle cross section area is assumed to be 1 018.10 H11002 H11002 m2 and the propane flue gas flow rate is 0.036 (Nm3/s).

\[
V_{\text{flue gas}} (\text{Nm}^3/\text{s}) = U_{\text{flue gas}} (\text{m/s}) \cdot A_{\text{nozzle}} (\text{m}^2)
\]

The Reynolds number of propane flue gas is calculated using Eq. (5), where the propane flue gas-density (ρP), -viscosity (μP), -velocity (U_P) and the SEN diameter (dN) are assumed to be 0.89 (kg/m3), 375.10 H11002 H11002 (kg/ms), 35 (m/s) and 0.036 m respectively.

\[
\text{Re} = \frac{\rho_P \cdot U_P \cdot d_N}{\mu_P}
\]

The calculated Reynolds number is 29 904. It defines that the propane flue gas flow in the SEN is turbulent. The Petukhov equation, as Eq. (6) shows, has been performed to calculate the Nusselt number by assumption of both the fully developed turbulent flow in the SEN and the SEN to be a smooth tube with a fraction factor (f) of 0.06. The calculated Nusselt number was 186 when n in Eq. (6) was supposed to be zero for gases and the Prandtl number (Pr) was 0.67.

\[
\text{Nu} = \frac{1.07 + 12.7 (f / 8)^{1/2}(Pr^{2/3} - 1)}{f} \left( \frac{\mu_P}{\mu_w} \right)^{n}
\]

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Figure 3 shows the cross section of the commercial Submerged Entry Nozzle (SEN). The initial temperature of the SEN and the ambient temperature are assumed to be constant at 298 K. The heat convection coefficient between the SEN and the ambient is assumed to be 10 (w/m2·K). The simulation has been performed for five points (A, B, C, D and E in Fig. 3) of SEN refractory materials from the inside surface (Point A) to the outside surface (Point E) with a 6.75 mm interval during 2 h.

The weight loss percent of each sample was calculated...
using Eq. (8) at a one second interval at controlled temperature and atmosphere with 6.8 (NL/min) argon, 0.64 (NL/min) carbon dioxide and 0.56 (NL/min) oxygen.

\[
\text{weight loss percent (wt\%) } = \left( \frac{m_i - m_a}{m_i} \right) \times 100 \ldots \ldots (8)
\]

where \( m_i \) is the initial mass and \( m_a \) is the actual mass of the investigated sample. The diagram of both weight loss percent and temperature versus time were plotted for each sample.

3. Results and Discussion

The produced \((4B_2O_3 \cdot BaO)\) glass powder as an additive material and the prepared samples after sintering, were examined using a FEG-SEM and a XRD. Furthermore, the pre-heating simulation results were evaluated to determine both the applying temperature profile and the controlled atmosphere chemical composition during experiments. Finally, the results of experimental trials were analyzed to evaluate the influence of different additives on the decarburization rate of the samples. Furthermore, the mechanisms of the additive- and carbon-oxidation were examined using a FEG-SEM and a XRD.

3.1. The Raw Materials and the Samples SEM Observations

The produced \((4B_2O_3 \cdot BaO)\) glass powder was examined using a FEG-SEM. The SEM observations and chemical analysis performed by Energy dispersive X-ray Spectroscopy (EDS) showed the formation of a homogenous glaze with a chemical composition shown in Table 3. The stoichiometric ratio of the elements in atom percentage for the produced powder is \([B]:[Ba]:[O]=36.38:4.53:59.09=8:1:13.04\). This ratio was found to agree with the theoretical ratio for \((4B_2O_3 \cdot BaO)\), which is \([B]:[Ba]:[O]=8:1:13\).

A sample containing 8 wt% \(ZrSi_2\) and 15 wt% \((4B_2O_3 \cdot BaO)\) glaze (Test 7 in Table 2) was selected for chemical composition determinations after a completed green body sintering. The sintered sample was first manually crushed in a mortar and thereafter grinded in a ball mill during 24 h using corundum balls. Figure 4 presents the X-Ray Diffraction Analysis (XRD) performed for the sample. Here, \(ZrSi_2\), \(ZrSi\), \(SiC\), \((4B_2O_3 \cdot BaO)\) and \((B_2O_3 \cdot BaO)\) were detected. \(ZrSi\) and \((B_2O_3 \cdot BaO)\) glaze were formed during sintering process while other compound existed in mixed raw materials. Figure 5 shows the FEG-SEM image of the same sample after sintering. An Energy Dispersive X-ray Spectroscopy (EDS) line scan was performed along the 65 \(\mu\)m long straight line shown in Fig. 5. Figure 6 shows the line scans for \(Ba\), \(Zr\), \(Si\), \(C\), \(O\) and \(Al\) elements along the line. The line scan analysis clearly revealed the coexistence of the glaze and \(ZrSi_2\) between 20–50 \(\mu\)m, as indicated by the vertical lines in Fig. 6. The \(ZrSi_2\) particle surface may be covered by the glaze so that the glaze may act like an oxygen barrier. Also, the covered glaze may lead to a decrease of the \(ZrSi_2\) oxidation rate. In addition, the arrows in Fig. 6 show the region with a high amount of silicon and carbon and a low amount of zirconium. The existence of oxygen near the arrow in oxygen chart may be attributed to the existence of the high amount of BaO at the same place. It may be concluded that SiC exists in this region. Whitehead and Page\(^{45}\) have also established the high tendency of

| Element | Weight\% | Atomic\% | Compound | wt\% |
|---------|----------|----------|----------|------|
| B       | 20.06    | 36.38    | B2O3     | 64.60|
| Ba      | 31.71    | 4.53     | BaO      | 35.40|
| O       | 48.23    | 59.09    |          |      |

Fig. 3. The Submerged Entry Nozzle (SEN) cross section and corresponding heat transfer simulated points (A, B, C, D and E).

Table 3. Energy dispersive X-ray spectroscopy (EDS) analysis of the \((4B_2O_3 \cdot BaO)\) glass powder.
SiC formation by the reaction between metallic silicon and ZrC, which thermodynamically was supposed to be more stable than SiC.

3.2. The Pre-heating Simulation Results

The simulated temperature profiles for points A, B, C, D and E (Fig. 3) are shown in Fig. 7. The simulation revealed the following results:

- The temperature profiles are almost the same for points A, B, C, D and E inside the SEN alumina/graphite refractory for the studied time of 7 200 s due to that the graphite has a high thermal conductivity.
- The point A temperature increases from 298 to 1 473 K (1 172 K temperature increasing) in 1 140 s. Furthermore, it takes 4 320 s for the same point to be heated from 1 473 to 1 626 K (153 K temperature increasing).
- The maximum reached temperature is 1 626.5 K.

It seems to be logical to save energy and time by heating the SEN up to 1 473 K because the heating rate decreases drastically above this temperature. The simulated temperature profile between 398–1 473 K of point A was selected for laboratory sample heating. The experimental apparatus in Fig. 2 was capable to perform different heating programs (ramp) with a constant heating rate. Therefore, the simulated temperature profile has been divided into four sections, each one with a constant heating rate.

Furthermore, the alumina tube situated inside the furnace in Fig. 2 can just tolerate the heating rate of about 15 K/min and it may crack at higher heating rates.

The diffusion of oxidizing components (oxygen and carbon dioxide) occurs in both injected gas and through pores in refractory material. At the same time, the diffusion of carbon monoxide through pores in refractory material are assumed to be the rate-controlling steps in decarburization reactions. Sasai and Mizukami\(^\text{15}\) suggested the Eq. (9) and Eq. (10) for the carbon oxidation rate as a function of the oxidizing components partial pressure. Equation (9) is a model for diffusion of oxidizing components in the injected gas and Eq. (10) is a model for diffusion of oxidizing components through the refractory pores.

\[
\frac{dr}{dt} \propto \frac{(P_{\text{oxygen},F} - P_{\text{oxygen},I})}{T} \quad \text{(9)}
\]

\[
\frac{dr}{dt} \propto \frac{(P_{\text{oxygen},I} - P_{\text{oxygen},R})}{T} \quad \text{(10)}
\]

where \( r \) is the reaction interface radius, \( t \) is the time, \( T \) is temperature, \( P_{\text{oxygen},I} \) is the oxidizing components partial pressure in injected gas, \( P_{\text{oxygen},R} \) is the oxidizing components partial pressure at the injected gas/refractory interface and \( P_{\text{oxygen},R} \) is oxidizing components partial pressure at the reaction interface. It can be concluded that the partial pressure of the oxidizing component decide the reaction rate of decarburization at each temperature for the same sample. The
longer holding time at a specific temperature may be compensated by reducing the oxidizing components partial pressure at the same temperature. Therefore, the partial pressure of injected oxygen and carbon dioxide were adjusted so that the total oxidizing components amounts, which the refractory materials were exposed to, were the same for both high and low heating rates. The heating rate during laboratory trials was 15 K/min.

Table 4 presents the oxidizing components amount and temperature profiles for both simulated- and laboratory trials calculations. The injected gases flow rates adjustments were performed using four brooks Sho-rate flow meters with R-2-15-B tubes (glass and Tantalum float) and R-2-15-AAA tubes (carboloy float). As Table 4 illustrates, the total amount of oxidizing components (oxygen and carbon dioxide) in the injected gases are almost the same for both simulated temperature profiles with different heating rates and laboratory trial temperature profiles. The carbon oxidation trials were performed for each sample given in Table 2 with temperature profile and gas components shown in Table 5.

### 3.3. The Influence of Different Additives on the Carbon Oxidation Rate

Figure 8 shows the weight loss versus time for Test 2, Test 3, Test 4 and Test 12 shown in Table 2. The negative values around 30 min for Test 2 and Test 3 can be attributed to the formation of zirconia and silica phases at temperatures higher than 737 K [16] and therefore the samples weight gain. Both samples (Test 2 and Test 4) contain 15 wt% ZrSi₂, whereas one contains 5 wt% glaze (4B₂O₃ · BaO) and 5 wt% B₂O₃ (Test 4). The weight loss value for Test 4 showed a very slight value decrease of about 1.17 units in comparison to the weight loss value for Test 2 after the experiment completion at 1 473 K. The comparison between Test 4 and 2 curves reveals a higher oxidation tendency in Test 4 than in Test 2 and it lasts until the temperature reaches about 1 273 K. After that, the two curves come very close. Also, at 1 473 K Test 4 shows a better oxidation re-
sistance. This result can theoretically be related to the green body sintering in Test 4, which led to volatilization of B$_2$O$_3$ and thereafter excessive open pores in the refractory materials. Also below 1 273 K, the oxygen diffusion ability into the refractory materials was facilitated due to the presence of the pores. Above 1 273 K, the (4B$_2$O$_3$·BaO) glaze melted, which by coexistence of an antioxidant led to a decrease of the oxidation rate. The decarburization resistance was enhanced most by additions of 15 wt% ZrSi$_2$ and 10 wt% glaze (4B$_2$O$_3$·BaO), presented as Test 3. This test showed a weight loss value reduction of about 5.25 unit in comparison to the weight loss value for Test 2. This may prove the existence value of a glaze material with a melting point not much higher than the carbon oxidation temperature (873–973 K), which is also stable at high temperatures. The comparison between the weight loss as a function of time for samples containing 15 wt% ZrSi$_2$ and 10 wt% (4B$_2$O$_3$·BaO) with sintering (Test 3) and without sintering (Test 12) clearly shows higher carbon oxidation resistance for the sintered sample. The heating of the green body (Test 12) leads to more carbon oxidation at temperatures under 1 273 K in comparison to the sintered sample. This can be related to the melting of the (4B$_2$O$_3$·BaO) powder during the sintering of the green body, which theoretically may lead to filling of the open pores in the green body. In addition, the glaze supply a better oxidizing-atmosphere barrier at temperatures below 1 173 K, while an un-sintered body is more exposed to an oxidizing-atmosphere before the glaze is melted. Figure 9 shows the weight loss percent for Test 5, Test 6 and Test 7 shown in Table 2. The comparison of Test 5 and Test 6, both containing 8 wt% antioxidant whereas one contains 10 wt% glaze (4B$_2$O$_3$·BaO) (Test 6), revealed a decarburization resistance enhancement of about 2.67% for Test 6. Test 7 containing 8 wt% ZrSi$_2$ and 15 wt% glaze (4B$_2$O$_3$·BaO) and Test 6 containing 8 wt% ZrSi$_2$ and 10 wt% glaze (4B$_2$O$_3$·BaO) showed insignificant differences during heating in an oxidizing atmosphere. Figure 10 shows the weight loss for Test 8 and Test 9 shown in Table 2. The comparison of the two samples both containing 4 wt% antioxidant, whereas one contains 10 wt% glaze (4B$_2$O$_3$·BaO) (Test 9), revealed a decarburization resistance enhancement of about 1.50% for the sample containing the glaze (Test 9). Figure 11 shows the weight loss percent for Test 10 and Test 11 (Table 2) both containing 2 wt% antioxidant whereas one contains 10 wt% glaze (4B$_2$O$_3$·BaO) (Test 11). The comparison of these samples revealed a very slight decarburization resistance enhancement of about 0.7% for Test 9.

The decarburized thickness layer of each specimen was measured by using the light optic microscopy. The measured thickness was compared to the decarburization thickness layer of the Refractory Base Material (RBM). Equation (11) defines the Decarburization Resistance Improvement in percent (DRI %).

\[
\text{Decarburization Resistance Improvement \% (DRI, \%)} = 100 \times \left(1 - \frac{a}{b}\right) \tag{11}
\]

Where \(a\) is the decarburization layer thickness of the antioxidant-containing sample and \(b\) is the decarburization layer thickness of the base refractory materials (RBM).

Figure 12 shows the DRI% for Tests 2–11. The sample with 8 wt% ZrSi$_2$ and 15 wt% (4B$_2$O$_3$·BaO) glass powder (Test 7) showed a carbon oxidation resistance improvement of 46.3 DRI% and this was the highest value. Test 4, which contained both B$_2$O$_3$ powder and (4B$_2$O$_3$·BaO) glass powder, showed less resistance in comparison with Test 3 containing just (4B$_2$O$_3$·BaO) glass powder. Also, the addition of (4B$_2$O$_3$·BaO) glass powder mostly enhanced the decar-
The sensitivity to temperature of the ZrSi2 containing refractory specimens is lower for a temperature increase of 300 K. The slight weight loss percentage increase of about 1% was revealed for samples containing 8 wt% ZrSi2. The addition of (4B2O3·BaO) glass powder showed almost no effect on the decarburization resistance for specimens containing more than 8 wt% ZrSi2. The addition of (4B2O3·BaO) glass powder showed almost no effect on the decarburization resistance for specimens containing 4 and 2 wt% ZrSi2.

Figure 13 shows the weight loss % vs. time for samples containing 15 wt% ZrSi2 and 15 wt% (4B2O3·BaO) decarburized at 1473 K and 1773 K respectively.

3.4. The Mechanisms of the Additive Oxidation and Decarburization

Gebwein et al.16) have studied the oxidation kinetics of ZrSi2 powder in flowing air using non-isothermal thermogravimetric (TG) analysis with heating rates of 10 K/min. The results showed that the oxidation may lead to formation of elemental silicon and an intermediate reaction product at temperatures above 1073 K and thereafter the oxidation of elemental silicon may proceed at temperatures above 1373 K as reaction 13 shows. Finally, the zircon formation may proceed at temperatures above 1373 K as reaction 13 shows. The reaction proceeds as long as the zirconium disilicide amount becomes zero at the reaction interface. At the absence of the zirconium disilicide, the carbon oxidation may be assumed to proceed at temperatures 873 to 1073 K as reactions 14, 15 and 17 show. The oxidation of metallic silicon may proceed at temperatures above 1073 K as reaction 13 shows. Finally, the zircon formation may proceed at temperatures above 1373 K. The zirconia formation may be accounted as the most important stage during which the volume expansion is considered to prevent the oxygen ingress. Furthermore, reaction 16 presents the oxidation of SiC formed during the green body sintering.

An X-Ray Diffraction Analysis (XRD) was performed for the sample containing 8 wt% ZrSi2 and 10 wt% (4B2O3·BaO) glaze powder (Test 6) after the decarburization laboratory trial completion at 1473 K. The results revealed the existence of both ZrSiO4 and (4B2O3·BaO) as shown in Table 5.

Region A

The atomic ratio of zirconium and silicon agrees with the ratio of the antioxidant addition in the prepared sample.

\[ \text{ZrSi}_2 = [\text{Zr}] : [\text{Si}] = [1] : [2] \]

Region A = [Zr] : [Si] = [1.11 : 22.09 = [1] : [1.99]

It can be concluded that this region constitutes of both ZrSiO4 and SiO2.

The reaction interface between the samples and the gas phase may be assumed to be circle for cylindrical samples in this study. Therefore, alumina, silica, graphite and zirconium disilicide may come into contact with the gas atmosphere at the reaction interface. Initially, oxygen reacts instantaneously with zirconium disilicide at 737 K to form ZrO2, SiO2 and metallic silicon as reaction 12 shows. The reaction proceeds as long as the zirconium disilicide amount becomes zero at the reaction interface. The absence of the zirconium disilicide, the carbon oxidation may be assumed to proceed at temperatures 873 to 1073 K as reactions 14, 15 and 17 show. The oxidation of metallic silicon may proceed at temperatures above 1073 K as reaction 13 shows. Finally, the zircon formation may proceed at temperatures above 1373 K. The zirconia formation may be accounted as the most important stage during which the volume expansion is considered to prevent the oxygen ingress. Furthermore, reaction 16 presents the oxidation of SiC formed during the green body sintering.

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\[ \text{ZrSi}_2 + (x-(x-y/2)+1)\text{O}_2 \rightarrow \text{ZrO}_2(2-y)\text{SiO}_4 + y\text{Si} \quad \text{at } T \geq 737 \text{K}^{16} \]

\[ \text{ZrO}_2 + (2-y)\text{SiO}_4 + y\text{Si} + \text{O}_2 \rightarrow \text{ZrO}_2 + 2\text{SiO}_2 \quad \text{at } T \geq 1073 \text{K}^{16} \]

\[ \text{C} + \text{O}_2 \rightarrow \text{CO}_2 \quad \text{at } T = 873 - 973 \text{K}^{16} \]

\[ \text{C} + 1/2\text{O}_2 \rightarrow \text{CO} \]

\[ \text{SiC} + 2\text{O}_2 \rightarrow \text{SiO}_2(2-y) + \text{CO}_2 \]

\[ \text{C} + \text{CO}_2 \rightarrow 2\text{CO} \]

\[ \text{ZrO}_2 + \text{SiO}_2 \rightarrow \text{ZrSiO}_4 \quad \text{at } T \geq 1373 \text{K}^{8} \]
Region B
The atomic ratio of zirconium and silicon does not agree with the ratio of the antioxidant addition in the prepared sample.
ZrSi₂=[Zr]:[Si]=[1]:[2]
Region B=[Zr]:[Si]=[15.07]:[16.60]=[1]:[1.10]
The analysis clearly shows the silicon content decrease, which can be attributed to the formation of SiC during sintering of the green body.

Region C
This region contains Zirconium and oxygen and almost no silicon. The refractory base material did not contain either metallic zirconium or zirconium oxide. This indicates the formation of ZrO₂ from ZrSi₂ additions. The absence of the silicon in this region may be related to the SiC formation during the sintering. The SiC is then transported away from the region by (4B₂O₃·BaO) glaze after reaching its melting point.

Region D
This region consists of high amounts of silicon, oxygen and aluminum. The aluminum oxide is from the refractory base material. Furthermore, silica is the oxidation product of SiC, as reaction 16 suggests. More specifically, the formation of silica according to reaction 16 may explain the high amount of silica at region D.

Figure 16(a) shows the FEG-SEM image of the ZrSi₂ powder used as antioxidant additive in this paper. As the figure shows, the particles sizes may vary between 5.86 μm and 21.49 μm. Figure 16(b) shows the image of a sample containing 15 wt% ZrSi₂ and 10 wt% (4B₂O₃·BaO) glass powder after decarburization at 1473 K. The ZrSi₂ particles sizes after oxidation may vary between 25.13 μm and 68.01 μm. The comparison between particles sizes in Figs. 16(a) and 16(b) may illustrate the oxidation and volume increasing of ZrSi₂ particles which had been situated between alumina particles as well as the formation of zircon (ZrSiO₄). This mechanism may lead to closing of the refractory open pores and thereafter the oxygen ingress prevention.

4. Conclusions
This work focused on the effects of ZrSi₂ additive on the carbon oxidation resistance of the alumina/graphite refractory materials used in Submerged Entry Nozzles. The laboratory trials temperature profiles were simulated using the ComSol software to perform the trials at non-isothermal heating conditions as it is for pre-heating of the Submerged Entry Nozzles. The pre-heating simulation was performed assuming the usage of a propane combustion torch with a fuel consumption of 10 kg/h and the flue gas temperature of 1773 K. The most important conclusions may be summarized as follow:

(1) The simulation results suggested an optimized pre-heating temperature of 1473 K for alumina/graphite refractory when the maximum reachable temperature is 1773 K.
(2) The ZrSi₂ acts as an antioxidant, to restrict the alumina/graphite carbon oxidation by reacting with the oxidizing components such as oxygen and carbon dioxide. The 121 vol% expansion due to the formation of the zircon (ZrSiO₄) from the ZrSi₂ during oxidation can close open

![Fig. 14. XRD analysis of sample with 8 wt% ZrSi₂ and 10 wt% (4B₂O₃·BaO) after the decarburization trial at 1473 K.](image)

![Fig. 15. FEG-SEM image of sample containing 15 wt% ZrSi₂ and 15 wt% (4B₂O₃·BaO) after decarburization trial at 1473 K, points A, B, C and D indicate the EDS analysis situations.](image)

![Fig. 16. SEM image for (a) ZrSi₂ and (b) sample containing 15 wt% ZrSi₂ and 10 wt% (4B₂O₃·BaO) after decarburization at 1473 K.](image)
pores of the refractory formed during oxidation of the graphite.

(3) The highest carbon oxidation resistance of the refractory was achieved by addition of ZrSi$_2$ at 8 wt% of the Refractory Base Material (RBM). The antioxidant addition showed almost no effect at 4 wt% and 2 wt% additions of RBM.

(4) The coexistence of ZrSi$_2$ and (4B$_2$O$_3$·BaO) glass powder presented a remarkable improvement of decarburization resistance for those samples containing 8 wt% and 15 wt% antioxidant of the RBM. The melting of the added glass powder led to filling of the refractory open pores formed during the green body sintering. The glaze acts as an oxidizing gas barrier.

(5) The (4B$_2$O$_3$·BaO) showed a better stability than a pure B$_2$O$_3$ glaze during sintering at temperatures higher than 1 273 K.

(6) The best decarburization resistance of the refractory was achieved by addition of 8 wt% ZrSi$_2$ and 15 wt% (4B$_2$O$_3$·BaO) glass powder to the RBM.

(7) The isothermal decarburization trials at 1 473 K and 1 773 K in 25 min revealed the less temperature sensitivity of the ZrSi$_2$-containing refractory materials at temperatures between 1 473–1 773 K.

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