Material Evaluation to Prevent Nozzle Clogging during Continuous Casting of Al Killed Steels

Y. VERMEULEN, B. COLETTI, B. BLANPAIN, P. WOLLANTS and J. VLEUGELS

Dept. Metallurgy and Materials Engineering, K. U. Leuven, Kasteelpark Arenberg 44, B-3001 Leuven, Belgium.
E-mail: Bart.Blanpain@mtm.kuleuven.ac.be

(Received on May 10, 2002; accepted in final form on July 18, 2002)

Al_2O_3 -carbon composite submerged entry nozzles (SEN) are used for continuous casting of steels. Although this material has excellent mechanical and thermal properties, it frequently leads to clogging. The purpose of our research is to find a suitable refractory material that can be used to coat SENs. This paper reports on the chemical compatibility of a number of potential refractory materials: Al_2O_3 , ZrO_2 , Al_2O_3 -carbon, SiO_2 and MgO with liquid steel, an amount of simulated inclusions and synthetic slag. For this purpose, an experimental laboratory procedure was optimised to simulate the nozzle behaviour during continuous casting. Al_2O_3 was found to give satisfactory results, and therefore a Al_2O_3 plasma coated Al_2O_3 -carbon material was also tested in the laboratory with good results.

KEY WORDS: continuous casting; aluminium killed low carbon steel; clogging; nozzle; refractory materials.

1. Introduction

The continuous casting process accounts for 90% of the world's steel output and is considered to be a mature technology.¹⁾ The submerged entry nozzle (SEN) plays a vital role in ensuring stable casting operations and slab quality. It is used to prevent oxygen and nitrogen pick-up and to achieve a desired steel flow in the mould. Clogging of SENs, *i.e.* a substantial reduction of the inner section of the nozzle due to the deposition of material consisting mainly of steel and inclusions on its inner wall, however remains a problem. Clogging eventually leads to a disruption of normal casting operations.

The refractory material of the SEN should have adequate chemical inertness and mechanical properties such as high temperature mechanical strength and thermal shock resistance.²⁾ Currently, mainly Al_2O_3 -carbon is used as the base material for the production of SENs, while fused silica and ZrO_2 -carbon occupy lower percentages of the SEN market.

Extensive scientific research has been carried out to investigate the mechanism of clogging (*e.g.* Refs. 3), 4)), to determine the interactions between the liquid steel flow and the refractory material of the SEN (*e.g.* Refs. 5), 6)) and to study the steel flow pattern in the nozzle (*e.g.* Refs. 7), 8)). A first reaction layer forms due to an increased oxygen activity near the refractory wall, causing the oxidation of Al_{Fe} to $\text{Al}_2\text{O}_3(\text{s})$. The increased oxygen activity can be caused by air leakage at the exchange mechanism, by air diffusion through the refractory material or by redox reactions in the refractory material.⁴⁾ This latter source originates from the reduction of SiO_2 , Na_2O and K_2O by the carbon in the refractory, leading to the formation of SiO , Na , K and CO gas. When CO and SiO gas reach the liquid steel, they will

raise the oxygen activity near the refractory wall. This causes the oxidation of Al_{Fe} , while Si and C will dissolve in the liquid steel.⁶⁾

Once this first alumina layer has been formed, deposition and accumulation of inclusions from the molten steel onto the inner wall of the SEN will occur.⁵⁾ The first alumina layer is considered to serve as an ideal substrate for this deposition process, as a rough refractory surface presents more energetically favourable sites for the deposition of alumina particles.⁹⁾ It is also reported that the deposited material consists mainly of Al_2O_3 and steel but may also contain smaller quantities of SiO_2 and CaO .^{4,10)} It is supposed that most of the inclusions are formed in the liquid steel.¹¹⁾ Once these inclusions adhere to the refractory wall, sintering occurs.

A number of possible ways to prevent clogging have been proposed, such as adaptation of the geometry of the nozzle,^{11–13)} Ca treatments,^{14,15)} or Ar injection.⁸⁾

In this study we report on laboratory experiments that simulate nozzle exposure and which allow to select a promising material to coat SENs. The present investigation focuses on the influence of the chemical composition of the refractory material on the chemical compatibility with liquid steel, inclusions and slag.

2. Experimental Procedure and Materials

The laboratory tests were performed in a resistance heated graphite furnace (W100/150-2200-50 LAX, KCE Sondermaschinen, Rödental, Germany). The samples were tested at 1550°C, the average casting temperature, for 150 min in an inert Ar-gas (Ar gas: Air Liquide, N39, 10 ppm O_2) atmosphere. After evacuation ($<10^{-1}$ Pa) the fur-

nace was filled with Ar gas to 3×10^4 Pa, which corresponded to 7.5×10^4 Pa at 1550°C . The apparent deviation from the ideal gas law is due to the limited hot zone within the furnace. An oxidising atmosphere is to be avoided since it causes oxidation of the liquid steel and the formation of CO gas in the case of carbon containing refractories. The P_{O_2} pressure near the inner wall of the SEN, in industrial practice, stands at approximately 10^{-8} Pa.⁴⁾ Therefore, the above mentioned conditions were selected because dynamic vacuum conditions are more difficult to correlate with industrial practice, as this causes the reduction of some components and leads to the decarburisation of carbon containing samples, as was observed in preliminary experiments. Thermodynamic calculations using the Ar gas composition and assuming an excess of C¹⁶⁾ indicate a P_{O_2} of approximately 4×10^{-20} Pa during the laboratory experiment. This oxygen potential will in practise be increased due to a reduction of the refractory samples.

For compatibility testing in the solid state, samples of the refractory material were prepared with dimensions of approximately $20 \times 10 \times 5$ mm. For the experiments with liquid steel, smaller specimens (approximately $10 \times 10 \times 5$ mm) were used. The specimens were placed in a corundum crucible. Three different tests were performed.

2.1. Interaction with Liquid Steel

Approximately 5 g of a low carbon, Al-killed, degassed steel (supplied by SIDMAR Steel Plant) was employed to perform the experiments. The aim of these tests was to investigate the chemical stability of the refractory material in contact with liquid steel.

2.2. Sintering Behaviour of Clogging Material on Refractory Material

Powder, consisting of a mixture of alumina particles and steel, was collected from the outer layer of clogging material present on a used SEN. The SEN originated from a 2 strand slab caster using stopper rod flow control and through which 5 heats of approx. 292 ton per heat of an LCAK steel grade had flowed. The alumina is present as corundum particles of which the size ranges between 1 and $5 \mu\text{m}$. Their shape indicates they were formed in the melt. The steel is present as droplets with a size ranging from 1 to 2 mm. The overall chemical composition of the collected clogging material was determined by X-Ray Fluorescence Spectroscopy (XRF Philips, PW2400) and is given in Table 1. To this purpose the powder was first crushed using a Retch RM 100 of which 0.3 g was subsequently fused with 6 g $\text{Li}_2\text{B}_4\text{O}_7$, 3 g and 3 droplets of LiBr_2 into a glass bead using a Pearl'X 3 (Philips). A quantitative routine was used with seven standards made of variable compositions of available standards: BS 100A and BS 101/3, of Al_2O_3 (ACROS; Art. 21570) and of Fe_2O_3 (MERCK; Art. 2924).

The purpose of these tests is to investigate the effect of the refractory material on the sintering behaviour of inclusions and to find out whether the inclusions sinter to the refractory material. To this purpose the refractory material is heated together with an amount of 'inclusions', collected from a used SEN.

2.3. Interaction with Slag

In these experiments a synthetic slag layer was placed on

Table 1. Chemical composition of inclusions collected from a used SEN, as determined by XRF.

Compound	[mass%]
Al_2O_3	53.78
Fe	43.95
SiO_2	1.39
CaO	0.53
MgO	0.24
TiO_2	0.11

Fig. 1. Overview of the experimental set-up used to simulate the influence of slag elements on the clogging behaviour of refractory materials.

the refractory material, as graphically presented in Fig. 1. The layer consists of two stacked powders of 0.4 g each. Powder 1 consists of collected clogging material with a small amount of slag components added, CaO (ALDRICH; Art. 24,856/8) and MgO (MERCK; Art. 5865), whereas powder 2 simulates an amount of poured slag. It consists of CaO and MgO because they proved to be very reactive slag components in preliminary experiments.

The goal of this test is to investigate the chemical stability of potential refractory materials with typical slag phases that may contact the inner wall of the nozzle.

The selected refractory materials are: Al_2O_3 , ZrO_2 , Al_2O_3 -carbon, fused SiO_2 and MgO (Table 2). The composition was obtained from the supplier, or determined by XRF (Philips, PW2400) in the case of MgO.

Additionally, a Al_2O_3 -C material that was plasma-coated with pure Al_2O_3 was also tested. The coating of approximately $200 \mu\text{m}$ was deposited with a Metco 10-MB system

using pure Al_2O_3 powder (HC-Stark). The coating was also densified at 1600°C for 2 h under an Ar atmosphere.

After the tests all heated material combinations were embedded in Epofix resin and subsequently ground, for SEM/EDS analysis (Philips XL-30 FEG). Polishing was not performed, as it was found to damage the refractory materials. The samples from the interaction experiments with liquid steel were embedded together with their crucible, as this could not be removed, and cut with a diamond saw, without further grinding or polishing.

To perform TEM-analysis (Philips CM-200 FEG) the samples were embedded in a resin (EPON 812) and ultramicrotomed (LKB ultratome) to a thickness of approximately 70 nm.

Table 2. Composition of the refractory materials used during the experiments.

Refractory Material	Al_2O_3 -graphite	Al_2O_3	Fused SiO_2	ZrO_2	MgO
Composition [mass%]					
Al_2O_3	62–66	>99.99	0.1–0.3	/	<1
C	19.5–24.5	/	/	/	/
SiO_2	3.75	/	> 99.5	/	<1
ZrO_2	4.60	/	/	94.8	/
MgO	0.37	/	Traces	/	96
BN	/	/	/	/	/
TiO_2	0.99	/	Traces	/	/
Si	1.03	/	/	/	/
Fe_2O_3	0.34	/	< 0.03	/	<1
CaO	/	/	< 0.2	/	2
Y_2O_3	/	/	/	5.2	/

3. Results and Discussion

3.1. Interactions with Liquid Steel

In all combinations, alumina inclusions are detected in the steel. These particles are also observed during the interaction between liquid steel and Al-free refractory materials, like ZrO_2 . It seems therefore that Al_2O_3 particles are formed *in-situ*. The dense Al_2O_3 crucible was eliminated as a possible source, as observation of the area close to the crucible wall revealed that the crucible was chemically stable. It would seem therefore that some reoxidation of the steel took place during the experiments.

No evidence for a chemical interaction zone could be found between the liquid steel and the Al_2O_3 -C refractory material (**Fig. 2(a)**). No steel infiltration in the refractory material was observed. Alumina particles—in addition to those observed in other combinations—are however found in the steel. The size and morphology of these particles matches well with that of the smaller ($<10\text{ }\mu\text{m}$) Al_2O_3 grains of the refractory material. It can therefore be concluded that the carbon in the refractory is partially dissolved and the loosened alumina particles are engulfed by the steel.

No interactions were observed between ZrO_2 and liquid steel and no pores were induced (**Fig. 2(b)**). Moreover, there are conditions of non-wetting between ZrO_2 and liquid iron (contact-angle = 122° ¹⁷⁾).

Between fused silica and liquid steel few interactions took place, although in some places a composition similar

Fig. 2. Electron microscopic images showing the reaction zone of the investigated refractory materials with steel: (a) Al_2O_3 -C; (b) ZrO_2 ; (c) SiO_2 , the arrow indicates a location where fayalite was found; (d) MgO and (e) Al_2O_3 .

Fig. 3. Electron microscopic images showing the reaction zones of the investigated refractory materials with inclusions: (a) $\text{Al}_2\text{O}_3\text{-C}$, the dashed line indicates the contact between inclusions and refractory material; (b) ZrO_2 ; (c) SiO_2 , the dashed line indicates the contact between the refractory material and the reaction phase area (for compositional information see also Table 3); (d) MgO , the dashed lines enclose the reaction zone (for compositional information see Table 4) and (e) Al_2O_3 .

to that of fayalite was found (Fig. 2(c)). XRD measurements revealed that the fused silica partially crystallised to tetragonal cristobalite. This was confirmed by TEM analysis, although some remanent fused silica was also noticed.

The MgO refractory disintegrated near the interface but no steel penetration in the MgO occurred (Fig. 2(d)). However Al_2O_3 , SiO_2 and MgO particles from the refractory material were found dispersed in the steel, which is facilitated by the partial disintegration of the MgO material.

Few or no interactions took place between Al_2O_3 and liquid steel and epoxy of the embedding material can be found at the interface as a result of the poor bonding between the two materials. Some evidence of slight erosion of the refractory was observed (Fig. 2(e)). As no new compounds are formed, it was however concluded that Al_2O_3 is chemically stable in contact with the liquid steel.

It can be concluded from these experimental observations that all the investigated refractories possess a good to excellent chemical stability in contact with liquid steel.

3.2. Interactions with Clogged Material

Inclusions are sintered to the surface of the $\text{Al}_2\text{O}_3\text{-carbon}$ refractory. A TiO_x phase has penetrated along the porosity of the refractory material (Fig. 3(a)). Because this

TiO_x phase is only observed near the reaction zone and because the TiO_x phase contains small amounts of Fe, it is concluded that the TiO_x originates from the inclusions. The sintered inclusions consist mainly of Al_2O_3 . The brighter areas in the inclusions contain small amounts of CaO (6.4 mass%) and MgO (2.7 mass%), originating from entrapped slag during pouring, while the sintered dark inclusions are pure Al_2O_3 . A dispersed fayalite phase ($2\text{FeO} \cdot \text{SiO}_2$) is also found in the inclusions. The Fe originates from the clogged material collected from a used SEN. The oxidation of Fe requires an increased oxygen concentration near the refractory material, which is also detected near the refractory wall of a SEN. This is confirmed by the proposed reaction scheme in the refractory material of an $\text{Al}_2\text{O}_3\text{-carbon}$ SEN^{3,4,6}:

resulting in the overall reaction:

A small amount of inclusions is attached to the ZrO_2 refractory (Fig. 3(b)), which results in a sintered layer of approximately $100\text{ }\mu\text{m}$. No enrichment of the ZrO_2 by Al or Fe, neither of the Al_2O_3 by Zr could be observed. Although some limited interaction between the ZrO_2 and the clogged material was observed, it is very unlikely to be of a chemical nature.

Fused silica partially transforms in cristobalite¹⁰⁾ and a reaction zone of approximately $150\text{ }\mu\text{m}$ forms, as shown in Fig. 3(c). Cracks are formed due to the difference in thermal expansion coefficient. In order to locate the initial contact plane between the SiO_2 refractory and the inclusions, a similar experiment was carried out using a ZrO_2 powder marker. The position of the inert marker after the experiment is indicated on Fig. 3(c).

On the cristobalite side of the interaction couple (phase A in Fig. 3(c) and Table 3), a white iron cordierite phase (phase B) is found in combination with phases containing mainly Al_2O_3 and SiO_2 (phases C and D). As the composition of phases C and D varies over a wide range and is outside that of the crystalline mullite solid solubility region in the binary Al_2O_3 – SiO_2 system, we assume these phases to be glasses. The glassy phase (phase C) close to the pristine cristobalite contains remarkably lower amounts of Al_2O_3 in comparison with phase D, which is closer to the initial interface. The phases C and D can be correlated to the constituent glass phases of the metastable immiscibility region reported in the SiO_2 – Al_2O_3 phase diagram.¹⁸⁾

On the inclusions side of the interaction couple, three phases can be differentiated; phase E, with the same composition as phase D, phase F which contains considerable amounts of FeO_x in addition to SiO_2 and Al_2O_3 and phase G, being large crystalline mullite crystals. The SiO_2 – Al_2O_3 – FeO_x phase (phase F) is actually a cristobalite solid solution that is formed directly from the melt during cooling.

Although the reaction zone is complex, a first attempt to understand the phase sequence has been made. During the heating process, a liquid with approximately the composition of the iron cordierite phase was formed at the initial contact plane from the inclusions and the refractory. At 1550°C , this liquid penetrated the silica refractory along the grain boundaries, providing a fast diffusion path for Si and Al. The inward diffusion of Al from the dissolved inclusions resulted in the formation of the Al_2O_3 – SiO_2 glass phases C and D. This glass phase is even extended as phase E in the melt on the inclusion side, as can be deduced from the growth direction. At the reaction front in the refractory, SiO_2 dissolves in the liquid iron cordierite and diffuses to the inclusion side resulting in the formation of a SiO_2 -rich melt (phase F) and the crystallisation of mullite (phase G).

Chemical interactions between the MgO refractory material and the inclusions resulted in a reaction layer with a thickness of approximately $100\text{ }\mu\text{m}$ (Fig. 3(d)). In the reaction layer Al_2O_3 , MgO and FeO are observed in two distinct sublayers. The layer close to the refractory contains 19 mass% MgO, 73 mass% Al_2O_3 and 8 mass% FeO, whereas the other layer is composed of 8 mass% MgO, 64 mass% Al_2O_3 and 28 mass% FeO. The amount of MgO and Al_2O_3 increases towards the refractory material side, whereas the FeO content decreases. The surface of the

Table 3. Chemical composition (mass%) of the phases found in the interaction zone between SiO_2 and inclusions (see also Fig. 2(c)).

Phase	Al_2O_3 [mass%]	SiO_2 [mass%]	FeO [mass%]	Corresponding Phase
A	0	100	0	Cristobalite
B	18.0 ± 0.4	42.0 ± 1.3	40.0 ± 1.6	Iron Cordierite
C	41 ± 13	58 ± 13	1 ± 1	SiO_2 – Al_2O_3 glass phase
D	56 ± 19	43 ± 17	1 ± 1	SiO_2 – Al_2O_3 glass phase
E	58 ± 17	41 ± 15	1 ± 1	SiO_2 – Al_2O_3 glass phase
F	19 ± 1	62 ± 3	19 ± 2	Cristobalite solid solution
G	72 ± 1	28 ± 1	0	Mullite

MgO refractory next to the reaction layer partially disintegrated and an Fe-rich phase penetrated the refractory material up to a depth of 300 to $500\text{ }\mu\text{m}$.

No sign of interactions was detected between the Al_2O_3 in the refractory and the inclusions (Fig. 3(e)). This observation indicates that pure and dense Al_2O_3 does not interact with Al_2O_3 inclusions and steel at laboratory conditions.

These laboratory simulations proved that pure Al_2O_3 exhibits no noticeable interaction with retrieved clogging material at 1550°C , whereas in the case of ZrO_2 , inclusions were found to adhere to the refractory material. The SiO_2 and MgO refractory are not chemically stable in contact with the retrieved clogging material at 1550°C .

3.3. Interactions with Synthetic Slag

At some locations in the Al_2O_3 –carbon refractory material, CaO originating from the synthetic slag penetrated up to a depth of approximately $400\text{ }\mu\text{m}$ (Fig. 4(a)). Near the interface Al_2O_3 ·CaO is formed. Moving further away from the interface into the refractory material, the CaO concentration decreases from 30.1 ± 1.9 mass% at $200\text{ }\mu\text{m}$ to 14.7 ± 1.5 mass% at $400\text{ }\mu\text{m}$.

The synthetic slag penetrated the ZrO_2 refractory, resulting in a reaction layer of approximately $200\text{ }\mu\text{m}$ (Fig. 4(b)). The reaction layer consists mainly of Al_2O_3 ·MgO and two ZrO_2 -phases with a different CaO content. At the interface with the synthetic slag, the Y_2O_3 -stabilised ZrO_2 (tetragonal) is converted into CaO· ZrO_2 .¹⁹⁾ Further away from the interface, a large grained ZrO_2 phase is formed with approximately 10 mass% CaO and 3 mass% Y_2O_3 . The formation of large grains, approximately $10\text{ }\mu\text{m}$, is typical for cubic zirconia, which in this case is stabilised by a mixture of CaO and Y_2O_3 , whereas tetragonal yttria-stabilised zirconia has a grain size well below $1\text{ }\mu\text{m}$.

The slag also penetrated the cristobalite refractory, resulting in a reaction layer of approximately $100\text{ }\mu\text{m}$, as shown in Fig. 4(c). In the reaction layer, 2 phases could be identified: a dendritic silica phase and a slag phase composed of 62.1 ± 2.7 mass% SiO_2 ; 11.6 ± 0.1 mass% MgO; 11.8 ± 0.5 mass% Al_2O_3 and 14.5 ± 0.6 mass% CaO. This slag phase has a liquidus temperature of 1540 K .²⁰⁾

The MgO refractory surface disintegrated at the initial reaction front and the refractory is penetrated along the grain boundaries by the synthetic slag leading to the formation of monticellite (Fig. 4(d)). Penetration depths of approximately 2 mm were observed.

The Al_2O_3 refractory reacted with the synthetic slag resulting in a reaction zone of approximately $100\text{ }\mu\text{m}$ thick, as shown in Fig. 4(e). The reaction zone consists of four different phases, summarised in Table 4. The phase (A)

Fig. 4. Electron microscopic images of the reaction zones of the investigated refractory materials with the synthetic slag: (a) $\text{Al}_2\text{O}_3\text{-C}$, the dashed lines indicate the slag permeation zone; (b) ZrO_2 , the dashed lines indicate the reaction zone (for compositional information see Table 5); (c) SiO_2 the dashed lines indicate the reaction zone; (d) MgO , the dashed line indicates the interface and (e) Al_2O_3 , the dashed lines indicate the reaction zone (for compositional information see Table 6).

Table 4. Chemical composition (mass%) of the phases found in the interaction zone between MgO and inclusions (see also Fig. 2(d)).

Phase	MgO (mass%)	Al_2O_3 (mass%)	FeO (mass%)
A	19.0 ± 2.4	73.0 ± 2.5	8.0 ± 4.7
B	8.2 ± 1.0	64.4 ± 3.6	27.5 ± 3.2

Table 5. Chemical composition (mass%) of the phases found in the interaction zone between ZrO_2 and synthetic slag (see also Fig. 3(b)).

	ZrO_2 (mass%)	CaO (mass%)	Y_2O_3 (mass%)
Phase A	87.9 ± 3.3	9.3 ± 1.2	2.8 ± 2.8
Phase B	67.8 ± 2.5	27.1 ± 1.4	5.1 ± 1.9

Table 6. Chemical composition (mass%) of the phases identified in the interaction layer between synthetic slag and pure Al_2O_3 (Fig. 3(e)).

Phase	Al_2O_3 [mass%]	CaO [mass%]	MgO [mass%]	Corresponding Phase
A	92.1 ± 0.7	7.9 ± 0.7	0	$6\text{Al}_2\text{O}_3 \cdot \text{CaO}$
B	79.1 ± 0.4	20.9 ± 0.4	0	$2\text{Al}_2\text{O}_3 \cdot \text{CaO}$
C	74.8 ± 2.0	0	25.2 ± 1.6	$\text{Al}_2\text{O}_3 \cdot \text{MgO}$
D	81.0 ± 1.3	19.0 ± 0.5	0	$2\text{Al}_2\text{O}_3 \cdot \text{CaO}$

found next to the refractory material consists of Al_2O_3 and small amounts of CaO , resembling the $6\text{Al}_2\text{O}_3 \cdot \text{CaO}$ phase. Subsequently, a very thin layer of $2\text{Al}_2\text{O}_3 \cdot \text{CaO}$, phase B, can be observed. Moving further towards the slag, $\text{Al}_2\text{O}_3 \cdot \text{MgO}$ (spinel, phase C) is detected and finally, $2\text{Al}_2\text{O}_3 \cdot \text{CaO}$ (region D) is detected close to the synthetic slag. The synthetic slag itself consists of three different phases: $2\text{Al}_2\text{O}_3 \cdot \text{CaO}$, $\text{Al}_2\text{O}_3 \cdot \text{MgO}$ and Fe-droplets.

Since new compounds can be formed between the slag components CaO , MgO and the refractory materials it is concluded that contact between them has a negative influence for all of the investigated materials.

3.4. Al_2O_3 Plasma Coated $\text{Al}_2\text{O}_3\text{-C}$

The previous results show that Al_2O_3 is the most resistant in contact with liquid steel and clogged material. $\text{Al}_2\text{O}_3\text{-C}$ is chemically much less inert, but has good mechanical properties and is thermal shock resistant. Therefore it would seem that a Al_2O_3 coated $\text{Al}_2\text{O}_3\text{-C}$ refractory materials could present a good solution. The material was tested in contact with liquid steel, clogging material and synthetic slag.

The sample with the as-deposited coating sintered with

Fig. 5. Electron microscopic image of the interaction between inclusions (A) and a densified Al_2O_3 (B) plasma coated Al_2O_3 -C (C) sample.

the clogging material. From this it was concluded that the reactions (1)–(4) that occur with the Al_2O_3 -C material were not sufficiently blocked by the coating. Therefore the coating materials was densified at high temperature. After this treatment no interaction with inclusions was found (Fig. 5). The densified material also withstood the contact with liquid steel well. Some liquid steel did however penetrate the coating in a few locations in the form of small steel droplets with a size of approximately $2\text{ }\mu\text{m}$. The reaction with synthetic slag is very similar as was described for the bulk Al_2O_3 .

4. Conclusions

Some Al_2O_3 grains are dispersed in the liquid steel due to carbon dissolution when Al_2O_3 -carbon contacts steel. Intense sintering occurred between this refractory material and inclusions, while calcium-aluminates are formed in contact with the slag phase. ZrO_2 does not react with liquid steel, but sintering occurred between inclusions and the refractory material. Ca enrichment of ZrO_2 takes place in contact with slag, forming a CaO - Y_2O_3 -stabilised zirconia or even $\text{CaO}\cdot\text{ZrO}_2$. After partial transformation of fused silica into cristobalite, due to the elevated temperatures, cracks appeared. Nevertheless, no interaction takes place with liquid steel. Silica however reacted intensively in contact with inclusions and synthetic slag. Although MgO disintegrates near the reaction interface, no steel penetration occurred. Nevertheless, the synthetic slag penetrated the refractory material and inclusions are sintered on the MgO

refractory. Al_2O_3 does not react with liquid steel nor with inclusions. In contact with a synthetic slag calcium-aluminates are formed. It is concluded that pure Al_2O_3 possesses interesting chemical properties as an anti-clogging material and with some tests using a Al_2O_3 coated Al_2O_3 -C material a possible solution to the clogging problem was indicated.

Acknowledgements

The authors would like to thank Dr. H. Kumar for his thermodynamical remarks and Ing. S. Goovaerts for the XRF-analysis.

REFERENCES

- 1) T. Smith: *Steel Times Int.*, **226** (1998), 389.
- 2) A. F. Dick, X. Yu, R. J. Pomfret and K. S. Coley: *ISIJ Int.*, **37** (1997), 102.
- 3) F. Hauck and J. Potschke: *Arch. Eisenhüttenwes.*, **53** (1982), 133.
- 4) J. Poirier, M. A. Guiban, P. Tassot, E. Hanse, B. Thillo and, P. Benson: Proc. Global Development of Refractories, The Technical Association of Refractories, Tokyo, (1995), 79.
- 5) Y. Fukuda, Y. Ueshima and S. Mizoguchi: *ISIJ Int.*, **32** (1992), 164.
- 6) K. Sasai and Y. Mizukami: *ISIJ Int.*, **34** (1994), 802.
- 7) F. G. Wilson, M. J. Heesom, A. Nicholson and A. W. Hills: *Ironmaking Steelmaking*, **14** (1987), 296.
- 8) K. G. Rackers and B. G. Thomas: 78th Steelmaking Conf. Proc., ISS, Warrendale, PA, (1995), 723.
- 9) K. Harold, A. Elksnitit and K. Oguri: Proc. Int. Symp. on Advances in Refractories for the Metallurgical Industries III, ed. by C. Allaire and M. Rigaud, CIM Met. Soc., Québec, (1999), 163.
- 10) Y. Vermeulen, B. Blanpain, P. Wollants, F. Haers, L. Peeters and C. Vercruyssen: Proc. 3rd European Conf. on Continuous Casting, The Spanish Committee of Technology of the Unión de Empresas Siderúrgicas-UNESID, Madrid, (1998), 1013.
- 11) S. N. Singh: *Metall. Trans.*, **5** (1974), 2165.
- 12) G. C. Duderstadt, R. K. Iyengar and J. M. Matesa: *J. Met.*, **20** (1968), 89.
- 13) W. Brandl and A. Sormann: Proc. 3rd European Conf. on Continuous Casting, The Spanish Committee of Technology of the Unión de Empresas Siderúrgicas-UNESID, Madrid, (1998), 714.
- 14) J. Kärjä, H. Nevala, U. Hintzen and M. Wiesel: *Stahl Eisen*, **113** (1993), 73.
- 15) N. Bannenberg: 78th Steelmaking Conf. Proc., ISS, Warrendale, PA, (1995), 457.
- 16) B. Sundman, B. Jansson and J. O. Andersson: *Calphad*, **9** (1985), 153.
- 17) A. W. Cramb and I. Jimbo: *ISS Transactions*, **11** (1990), 67.
- 18) S. H. Risbud and J. A. Pask: *J. Mater. Sci.*, **13** (1978), 2449.
- 19) H. M., Ondik and H. F. McMurdie: Phase Diagrams for Zirconium and Zirconia Systems, 1st Ed., The Amer. Ceram. Soc., Westerville, OH, (1998), 45.
- 20) FactSage software, <http://www.factsage.com>, accessed to February 6.