CORROSION MECHANISMS OF ZIRCONIA/CARBON BASED REFRACTORY MATERIALS BY SLAG IN PRESENCE OF STEEL

Filippo Cirilli, Antonello Di Donato, Umberto Martini, Patrizia Miceli, Philippe Guillo, Jose Simoes, Yi Jie Song

Zirconia is usually utilised in Submerged Entry Nozzle (SEN) in the slag contact zone, because of its high resistance to corrosion. However inconsistency of component performance and apparently erratic behaviours, in terms of corrosion rate, are frequently experienced. An important cause of the unexplained variability of component performance is the typical trial-and-error approach used to develop materials for the specific applications, and the "Darwinian selection" for the choice of the most suitable material despite the fact that a number of studies are available in literature. As a matter of fact, although almost all the mechanisms that have been proposed are based on some form of cyclic mechanism where the oxide is attacked by the slag and the exposed graphite is then attacked by the metal, contradictory conclusions can be often found about specific features. It is not to be excluded that contradictory results could be dependant on the experimental conditions used.

In this paper laboratory experiments have been carried out, using together slag and steel, in order to clarify their role on the global corrosion mechanism. The results showed that, besides the dissolution of carbon in steel and oxide in slag, other phenomena contribute to the corrosion. In particular the experiments put in evidence the critical role of steel in dissolving the products of reactions between slag components and carbon, pushing the attack of slag to carbon. The consequence is that the corrosion phenomenon is complex, and parameters such as activity of slag components, porosity of refractory matrix, characteristics of carbon material are involved in the tendency of the carbon to react with slag, hence on the global corrosion rate.

KEYWORDS: zirconia, continuous casting, Submerged Entry Nozzle, SEN, corrosion

INTRODUCTION

Zirconia is usually utilised in Submerged Entry Nozzle (SEN) in the slag contact zone because of its high resistance to corrosion. The occurrence of SEN corrosion is often the phenomenon determining the duration of the casting sequence. The steelmaker need is the availability of refractory materials at high resistance against corrosion, in order to make long sequences avoiding unforeseen stops of the casting operations. However inconsistency of component performance and apparently erratic behaviours, in terms of corrosion rate, are frequently experienced.

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Several corrosion mechanisms of zirconia/carbon refractories are available in the literature, taking into account the role of the two main different refractory components, zirconia and graphite.

All the mechanisms that have been proposed for attack of SENs are based on some form of cyclic mechanism [1,2,3]: the oxide component of the nozzle (zirconia) dissolves into the slag; as a consequence graphite remains exposed. Then a change in mould level brings this graphite into contact with the steel where it dissolves very rapidly, leaving refractory oxides exposed. The process then starts again leading to global refractory corrosion.

Hauck and Potschke [4] found two weak points in this type of cyclic mechanism:

1) fluctuations in the meniscus are less than the extent of the wear zone on nozzles
2) graphite dissolves more readily in the steel than the oxide in the flux; for this reason corroded nozzles would be expected to exhibit a network of exposed alumina or faster erosion in the steel than in slag.

To clarify the mechanism of corrosion they performed corrosion experiments with a rotating finger and found that there was always a slag film between the metal and the refractory in the eroded zone. According to their investigation the corrosion mechanism is based on dissolution of the refractory oxide phase dissolve in the flux and the carbon oxidation by iron oxide in the flux. They concluded also that Marangoni stirring at the slag/metal/refractory interface was one dominant factor.

Mukai et al. [5] further investigated the cyclic mechanism to identify the controlling step in refractory corrosion. For steels with low carbon levels the dissolution of the oxides in the slag is the rate determining step, because carbon dissolution into the steel is very rapid. This can explain the better performances in term of corrosion resistance of zirconia respect to alumina.

In case of high carbon levels into the steel (where high in this work means close to saturation) the rate controlling step is the carbon dissolution.

Moreover they proposed that the slow step in the process is the dissolution of the oxide phase, which is consistent with the superior performance of zirconia graphite over alumina graphite.

They also found that oxidation influenced the rate of attack and suggested that this was related to the agitation caused by liberation of CO. By killing their steel with aluminium, they eliminated the stirring effect of CO evolution.

The effect of atmosphere on corrosion rate was investigated by Dick et al [6]. They performed corrosion tests under argon and air atmosphere and they found much greater attack in the presence of air. They concluded that an important role in material corrosion is played by oxidation of the carbon.

According to Dick et al [1] oxygen activity in the steel plays an important role.

They noticed that steels with low oxygen potential caused the same wear rate and showed no function of carbon content until, at very high carbon levels, a decrease in wear rate was observed.

They concluded that in the Al-killed steels with low to intermediate carbons, the oxygen activity is controlled by the aluminium so the wear is not a function of carbon content. At very high carbons the oxygen activity is controlled by carbon and is below that fixed by the aluminium.

Other authors investigated the role of the stabilising agent of zirconia, which is commonly calcia. During interaction with slag, CaO present in zirconia grains as stabilising agent may be lost. Oki and coworkers [7 - 9] found that CaO present in zirconia grains react with oxides present in refractory additives causing the destabilisation of cubic zirconia and formation of monoclinic zirconia, resulting in the break up of the zirconia grains.

According to Dick et al [1], this mechanism can not be entirely correct as monoclinic zirconia is not stable at casting temperature regardless of composition. The CaO reaction does cause destabilisation, but it is the formation of liquid films such as calcium silicate at the grain boundaries that affects the attack rather than the stability of cubic zirconia.

Heikkinen et al [10] investigated the wear mechanism by measuring the wetting angle between molten steels and slags and ZrO_2-C-refractories. Depending on steel grade, the wettability of the refractory is increases after interaction with he slag. The wetting angle between mould powder slag and refractory material could not be measured because slag dissolved into the refractory material completely in only 1 – 3 minutes.

For both these observations they confirmed that the operating corrosion mechanism is the one in which the graphite is dissolved in steel while the ZrO_2 grains are destroyed due to the destabilising effect of slag that dissolves CaO from the refractory.

In this work a specific investigation has been performed on calcia stabilised zirconia in order to study the operating mechanism of corrosion when steel, slag and refractory are simultaneously in contact.

EXPERIMENTAL

Specific high temperature tests of interaction among steel, slag and refractory have been designed.

The objective of the tests is to investigate the corrosion mechanisms of zirconia and the role of each components of the system (oxides of the slag, liquid metallic phase and refractory constituents). In this work, three slags with different chemical composition have been used for corrosion test of the same refractory material immersed in liquid Fe. In what follows details of the materials, apparatus and experimental procedure are reported.

MATERIALS

-Refractory

The refractory material is a commercial ZrO_2-C refractory with CaO-PSZ (partially stabilised zirconia) grains. Chemical composition of the refractory is given in Tab. 1.

ZrO_2 [%]	CaO [%]	SiO_2 [%]	Al_2O_3 [%]	C [%]
74.0	3.0	2.0	1.0	20.0

Tab. 1

Composition of refractory.

Composizione del refrattario usato per i test sperimentali.

-Steel

To avoid the effect of interaction with slag and steel components, tests have been carried out using high purity iron, having the chemical composition reported in Tab. 2.

Fe [%]	C [%]	S [%]	Mn [%]
99.94	0.0120	0.0025	0.0170

Tab. 2

Chemical composition of iron used for experimental tests.

Composizione chimica del ferro usato per i test sperimentali.

-Slags

A large variety of casting powders, with different chemical composition, in used in continuous casting of steel. The composition of a casting powder is determined by several factors. The main ones are the steel grade, the casting speed, the type and size of cast product. As a consequence, the slags formed from casting powder can exhibit a variety of chemical properties, with consequence on the predominant corrosion michanism.

In this experimental activity synthetic slags, starting from pure materials have been used. The slag compositions have

	CaO [%]	SiO_2 [%]	Al_2O_3 [%]	MgO [%]	MnO [%]	Na_2O [%]
Slag 1	13	56	9	2	17	3
Slag 2	22	33	38	2	0	5
Slag 3	32	25	32	4	0	7

Tab. 3

Chemical composition of the slags used for the tests.

Composizione chimica delle scorie usate per i test sperimentali.

	a_{CaO}	a_{SiO2}	a_{Al2O3}	a_{MgO}	a_{MnO}	a_{Na2O}
Slag 1	0.002	0.694	0.081	0.012	0.064	3 E-8
Slag 2	0.005	0.208	0.991	0.013	-	3 E-6
Slag 3	0.082	0.128	0.736	0.035	-	5 E-6

Tab. 4

Calculated activity of slags components at 1550°C referred to the standard state of pure oxide (by Thermo-Calc™).

Attività dei componenti della scoria calcolate a 1550°C e prendendo come stato standard l'ossido puro (i calcoli sono stati fatti conThermo-Calc™).

not been fixed with the objective to reproduce the composition of casting powder, but to put in evidence the role of slag properties. According to this concept, three slags have been produced, having the following characteristics:
1. high SiO_2 and MnO activity
2. high SiO_2
3. high CaO activity
The complete slag compositions are reported in Tab. 3.
The chemical activity of the slags components, referred to the standard state of pure oxides, has been calculated with the thermodynamic code Thermo-CalcTM at the test temperature of 1550°C. The calculated values are reported in Tab. 4.

Description of experimental apparatus and procedure

The experimental tests were carried out in an electrical furnace, with graphite heating elements, under Ar atmosphere. The refractory samples were cut as rods of 2 cm of diameter and 5 cm length. For each test, an alumina crucible was filled with pure iron and heated up to the temperature of 1550°C. When the iron was completely melted, the furnace was open for adding the slag to the crucible and for putting the sample inside the furnace up to 10 cm above the crucible, to be preheated before submerging. Then, after complete slag melting and sample pre-heating (typically 5 minutes), the refractory rod was lowered inside the crucible so to be in contact with the liquid iron and the slag.
Fig. 1 shows a scheme of the experimental apparatus.
The duration of each test was 30 minutes. At the end of the test, the furnace was switched off, the sample left submerged and cooled under Ar flow.
After cooling and solidification, the crucible was cut and samples of refractory in contact with iron and slag were taken and submitted to Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS) investigation.

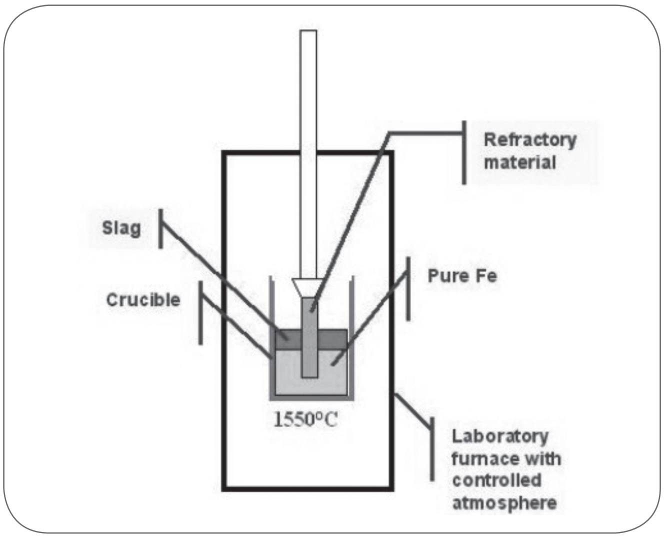


Fig. 1

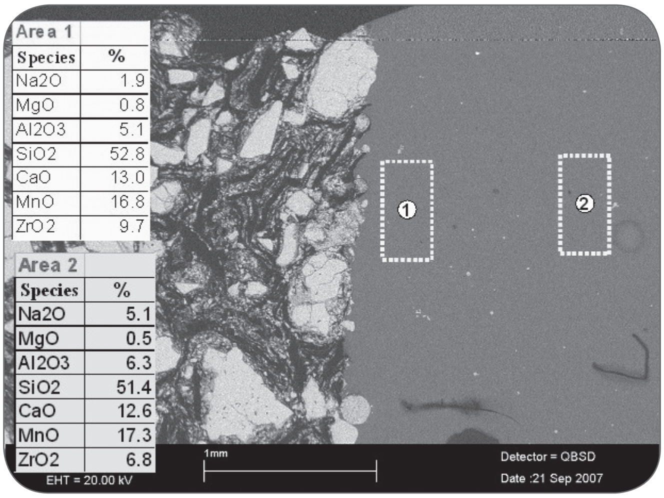
Scheme of the experimental apparatus used for the experimental tests.

Composizione del refrattario usato per i test sperimentali.

RESULTS

The investigation has been focused on the type and extent of the predominant interaction that occurs at the interface between the refractory and molten phases depending on the slag used. As already published in literature, the following phenomena have been observed on the refractory material after all the performed tests. They are:
- Graphite consumption: this occurs in general where the refractory is in contact with the metallic phase. A layer is formed in which the slag takes the place of the graphite and surrounds the zirconia grains. In what follows, this layer is called "decarburised layer".
- Slag penetration: the slag can penetrate through the refractory carbonaceous matrix.
- Structure degradation of ZrO_2 grains: this takes place in the grains that are in contact with the slag and can be observed in different forms, like simple cracks of the grain or complete crushing.

The extent of each phenomenon was different, depending on



Area 1	
Species	%
Na2O	1.9
MgO	0.8
Al2O3	5.1
SiO2	52.8
CaO	13.0
MnO	16.8
ZrO2	9.7

Area 2	
Species	%
Na2O	5.1
MgO	0.5
Al2O3	6.3
SiO2	51.4
CaO	12.6
MnO	17.3
ZrO2	6.8

Fig. 2

Refractory sample appearance after test with slag 1 at the slag contact level. EDS analysis performed on areas 1 and 2 of the slag.
Aspetto generale del refrattario dopo il test con la scoria 1 nella zona di contatto con la scoria N.1. Nelle zone indicate in figura con (1) e (2) è stata fatta l'analisi EDS.

the slag composition used for the test. The results of each experiment are reported in the following.

Results of test with slag 1

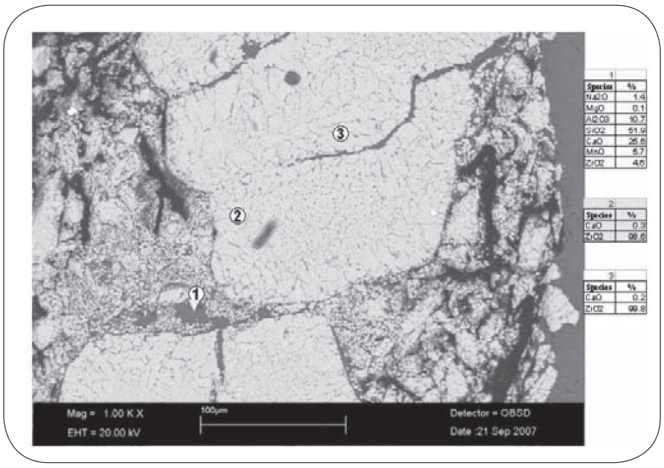
Fig. 2 reports a zone of the border of refractory in contact with the slag 1. The photo shows the upper part of the sample, which was in contact with the slag. EDS analysis performed on the slag at two different distances from the refractory border shows that the slag composition differs from the original for the presence of ZrO_2 coming from dissolution of refractory grains. The decreasing ZrO_2 concentration from area 1 to area 2 in Fig. 2 is due to the diffusion of zirconia into the slag.

Fig. 3 reports a magnification of Fig. 2. The zirconia grains appear drastically modified after interaction with the slag. The slag penetrated through the grains and this led to a progressive degradation of the coarse grains structure, whilst the finer grains were completely broken and dispersed into the slag.

The EDS analysis performed on the slag penetrated through the refractory shows an increase in CaO percentage to 26% respect to the initial value of 13 % (point 1 of Fig. 3). The CaO increase is due to complete CaO loss of the whole grains (as revealed by EDS analysis in point 2 and point 3 of Fig. 3).

Fig. 4 reports the appearance of the refractory below the liquid iron/slag contact level. A layer of slag impregnation, where graphite has been completely replaced by the slag is visible and has been indicated in Fig. 4. Beyond this layer, the slag penetrates through the refractory as shown by Fig. 5. EDS analyses show a decrease in MnO content of the penetrated slag.

Again, ZrO_2 grains in contact with the slag showed structure degradation and CaO loss; moreover a layer of slag impregnation, where graphite has been completely replaced by the slag is visible. Beyond this layer, the slag penetrates through the refractory



1	
Species	%
Na2O	1.4
MgO	0.1
Al2O3	10.7
SiO2	51.9
CaO	25.6
MnO	6.7
ZrO2	4.6

2	
Species	%
CaO	0.3
ZrO2	99.6

3	
Species	%
CaO	0.2
ZrO2	99.8

Fig. 3

Zirconia grain degradation of refractory interacting with slag 1 at the slag contact level.
Ingrandimento di Figura 2 che mostra la degradazione dei grani di zirconia del refrattario, nella zona di contatto con la scoria N. 1.

Results of test with slag 2

Fig. 6 reports the general appearance of the refractory border in the upper part of the sample in contact only with the slag. Zirconia dissolution from the refractory and diffusion into the slag are shown by EDS analysis performed in points 1 and 3 close to the refractory and in point 2 inside the slag.

Penetration of slag 2 inside the refractory is shown at higher magnification in Fig. 7. Slag 2 reacted with zirconia grains at the refractory border. Here, the coarse zirconia grains underwent structure degradation at the borders while the inner part of the grains did not show slag penetration.

Fig. 8 shows a magnification of a coarse zirconia grain in contact with the slag and the EDS analysis performed both on grain and slag. CaO was still present with the original concentration of 3 - 4 % inside the inner part of the grain where the slag did not penetrate. At the grain border, where structure degradation is evident, CaO was partially loss into the pene-

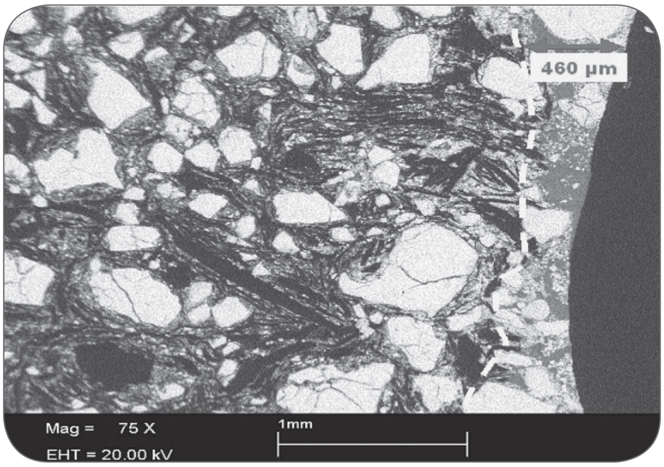
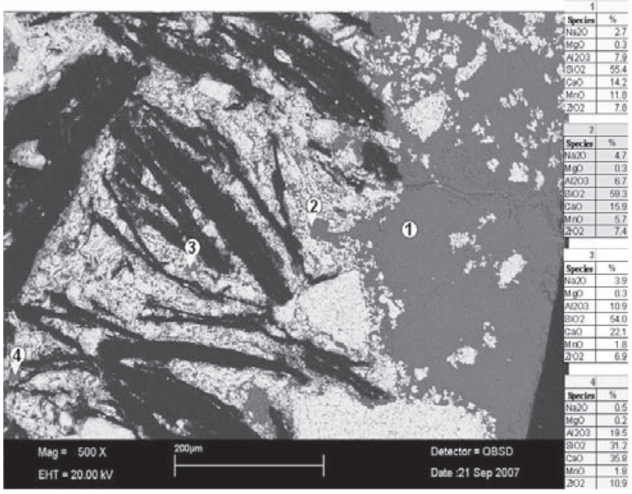


Fig. 4

Refractory sample appearance after test with slag 1 below the liquid iron/slag contact level. Decarburised layer is visible.
Aspetto generale del refrattario nella zona di contatto con l'acciaio dopo il test con la scoria N. 1. Lo strato decarburato è ben visibile in figura.



1	
Species	%
Na2O	2.7
MgO	0.3
Al2O3	7.9
SiO2	55.4
CaO	14.2
MnO	11.8
ZrO2	7.8

2	
Species	%
Na2O	4.7
MgO	0.3
Al2O3	6.7
SiO2	59.3
CaO	15.9
MnO	5.7
ZrO2	7.4

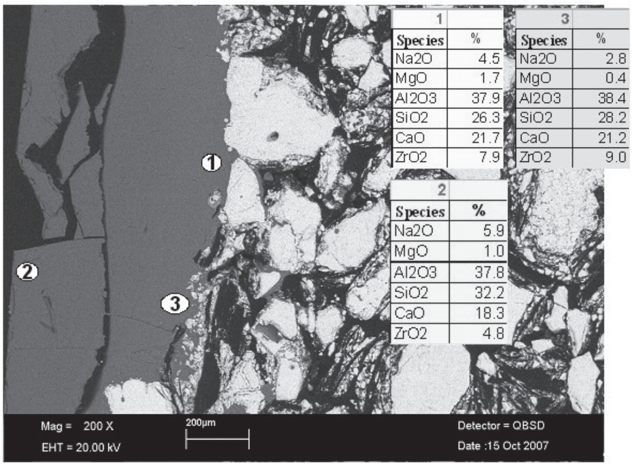
3	
Species	%
Na2O	3.9
MgO	0.3
Al2O3	10.9
SiO2	54.0
CaO	22.1
MnO	1.8
ZrO2	6.9

4	
Species	%
Na2O	0.5
MgO	0.2
Al2O3	19.5
SiO2	31.2
CaO	35.8
MnO	1.8
ZrO2	10.9

▲ Fig. 5

Penetration of slag 1 inside the refractory below the liquid iron/slag contact level. EDS analyses performed on penetrated slag.

Penetrazione della scoria N. 1 all'interno del refrattario al di sotto della zona di contato con la scoria. L'analisi EDS è stata fatta sulla scoria penetrata a diverse profondità all'interno del refrattario.



1	
Species	%
Na2O	4.5
MgO	1.7
Al2O3	37.9
SiO2	26.3
CaO	21.7
ZrO2	7.9

3	
Species	%
Na2O	2.8
MgO	0.4
Al2O3	38.4
SiO2	28.2
CaO	21.2
ZrO2	9.0

2	
Species	%
Na2O	5.9
MgO	1.0
Al2O3	37.8
SiO2	32.2
CaO	18.3
ZrO2	4.8

▲ Fig. 6

Refractory sample appearance after test with slag 2 at the slag contact level.
EDS analysis performed on points 1, 2 and 3 of the slag.

Aspetto del refrattario nella zona di contatto con la scoria N. 2 dopo il test sperimentale.

trated slag in contact with the grain. Analysis of the slag in point 2 of Fig. 8 indicates CaO concentrations of about 30 %, while the starting value was about 20 %.

Fig. 9 reports the appearance of the refractory below the liquid iron/slag contact level. In this case the average thickness of slag impregnation layer is less than 200 µm, and the extent of structure degradation is less than that remarked with slag 1.

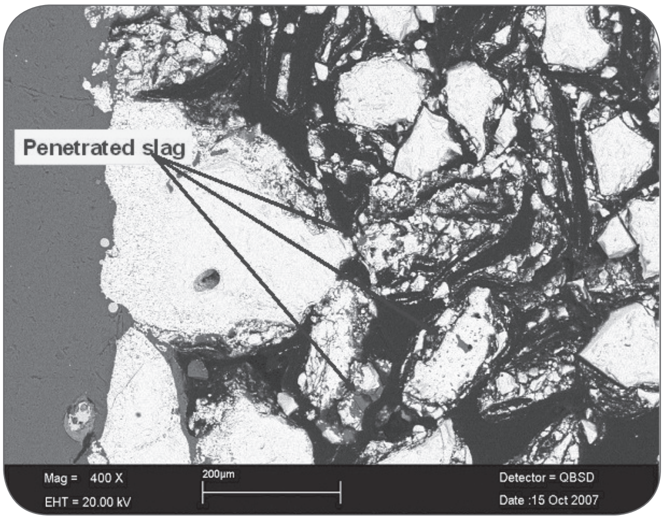
Results of test with slag 3

Fig. 10 shows the appearance of the refractory interface in contact with slag 3.

Zirconia grains are attacked by the slag, but the extent of the interaction is less evident respect that observed with slags 1 and 2. The slag analysis carried out on near the zone of the interface (see the zone 1) shows that the slag composition did not change in a significant way. The presence of dissolved ZrO_2 in the slag (up to 4÷5% wt.) has been remarked.

It is certainly caused by the degradation phenomena that affect the ZrO_2 grains that are in the zone of the refractory borderline. Anyway, with slag 3 only the smaller grains are attacked by the slag, while the larger ones are not significantly modified after the experimental test.

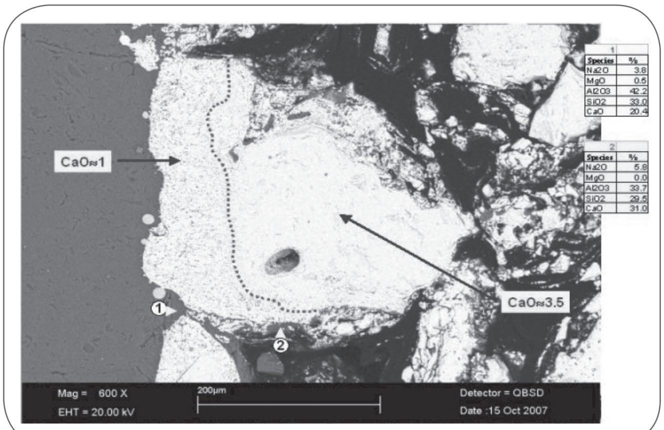
Fig. 11 reports the appearance of the refractory border in the liquid iron/slag zone. The layer of slag penetration is in the



▲ Fig. 7

Penetration of slag 2 inside the refractory at the slag contact level.

Penetrazione della scoria N. 2 all'interno del refrattario.



1	
Species	%
Na2O	3.8
MgO	0.6
Al2O3	42.2
SiO2	33.0
CaO	20.4

2	
Species	%
Na2O	5.8
MgO	0.0
Al2O3	33.7
SiO2	29.5
CaO	31.0

▲ Fig. 8

Structure degradation at the border of a coarse ZrO2 grain in contact with slag 2 at the slag contact level. EDS analysis performed on the grain and on points 1 and 2 of the slag.

Decadimento della struttura dei bordi dei grani di zirconia dopo interazione con la scoria N. 2. L'analisi EDS è stata fatta sui punti (1) e (2) indicati in figura.

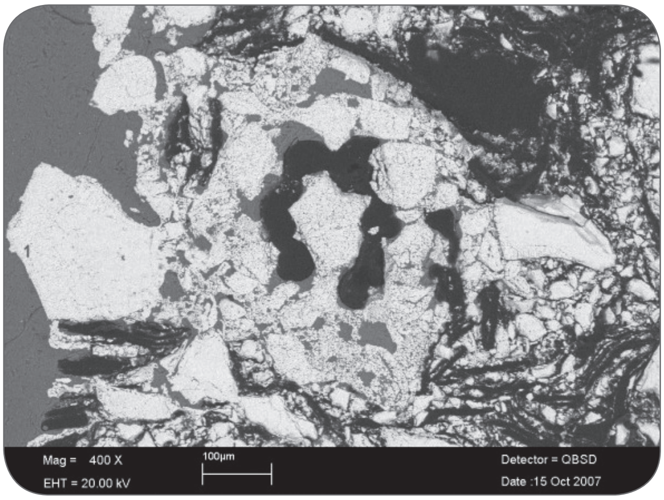
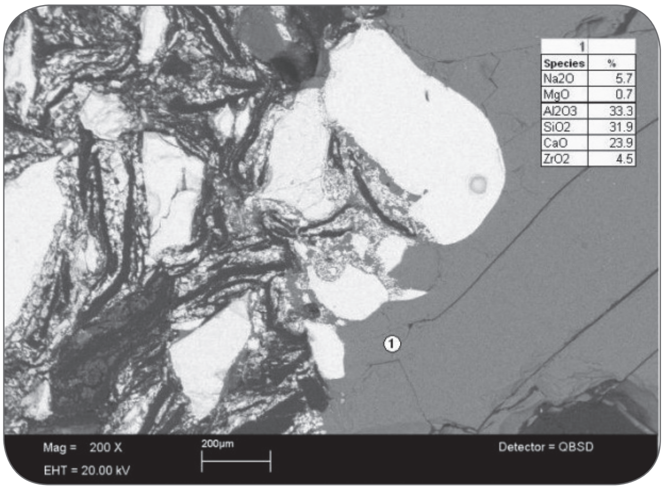


Fig. 9 **Refractory sample appearance after test with slag 2 below the liquid iron/slag contact level.**

Aspetto generale del refrattario dopo il test con la scoria N. 2, al di sotto della zona di contatto con la scoria.



1	
Species	**%**
Na2O	5.7
MgO	0.7
Al2O3	33.3
SiO2	31.9
CaO	23.9
ZrO2	4.5

Fig. 10 **Refractory sample appearance after test with slag 3 at the slag contact level. EDS analysis performed on points 1 of the slag.**

Aspetto del refrattario dopo il test con la scoria N. 3 nella zona di contato con la scoria. L'analisi EDS è stata fatta nel punto (1).

range 200-250 μm.

DISCUSSION

The following phenomena have been individuated as a global result of simultaneous interaction of the refractory with liquid iron and slag:
- Graphite consumption
- ZrO_2 grains degradation
- Slag penetration

Graphite consumption

To this phenomenon are observed in all the tests, but at different extent for the different slags.

It is known that graphite consumption can be due either to direct dissolution of C in the metallic phase or to the reaction of the graphite with reducible slag components, according to the following reactions [13-15]:

$$SiO_2 + C \rightarrow SiO + CO \qquad (1)$$

$$MnO + C \rightarrow Mn + CO \qquad (2)$$

Concerning the direct dissolution of C in the metallic phase, although it has not been measured in our tests, it can be assumed that the extent of phenomenon is the same in all the performed tests. Hence, the different thickness of the decarburised layer found in the three cases depends on the slag used. As already mentioned, the graphite consumption occurs only in the zones below the liquid iron/slag level. An explanation is that, according to reactions (1) and (2) the produced gaseous species SiO and CO and metallic Mn dissolve into the liquid iron shifting the reactions towards decarburation. In other words, the presence of the liquid metallic phase is necessary for the occurring of the graphite consumption; the extent of the phenomenon depends on the slag characteristics. From results of our tests, the higher activity of reducible oxides as MnO and SiO_2, the thicker the decarburised layer. Slag 1 resulted to be the more aggressive from this point of view due to the presence of MnO that is remarkable decreased in the penetrated slag as shown by Fig. 5 (points 3 and 4), and the highest SiO_2 activity as reported in Tab. 4.

ZrO_2 grains degradation

Phenomena involving ZrO_2 grains in contact with the slag are dissolution and grain structure degradation.

Dissolution has been observed in all the tests. This phenomenon has been widely investigated by several authors [1-3, 5, 11] as the most important cause of refractory corrosion, but the effect of slag composition on ZrO_2 grain structure degradation has not been completely clarified yet.

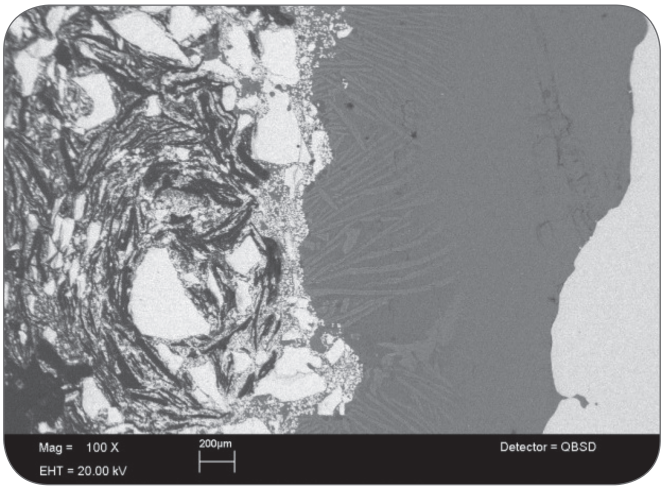


Fig. 11 **Refractory sample appearance after test with slag 3 below the liquid iron/slag contact level.**

Aspetto generale del refrattario dopo test con la scoria N. 3, in corrispondenza della zona di contatto con l'acciaio.

As a matter of fact, the degradation of the grain structure plays an important role in the corrosion of the material. In fact, grain degradation is accomplished by the slag penetration through the material and the loss of portions of ZrO_2 grains after their crushing.
Grains degradation occurred with all the three slags. Results from SEM observations showed that in general the grain degradation is associated with the loss of the stabilising agent CaO [12] as confirmed by the absence of CaO in the crushed grains and by the enrichment in CaO of the slag surrounding them. It follows that the extent of CaO dissolution from the grain into the slag can depend on slag characteristics, in particular on CaO activity in the slag or, in other words, on basicity index CaO/SiO_2.
In our tests, the extent of grain degradation is significantly different depending on the slag used: structure degradation occurs in the whole ZrO_2 grain in the case of slag 1, while it takes place mainly on the border of the grain in the case of slag 2 and with even less extent in the case of slag 3.
From a qualitative evaluation, the extent of grains degradation has the following order:

Extent of grain degradation: Slag 1 >> Slag 2 > Slag 3

that is in agreement with the increasing basicity index of the three slags.

CaO and SiO_2 activities reported in Tab. 4 for the three slags have the following orders:

CaO activity: Slag 1 < Slag 2 < Slag 3

SiO_2 activity: Slag 1 >> Slag 2 > Slag 3

Again slag 1 results to be the most aggressive also regarding the extent of grain structure degradation due to the high silica activity and low calcia activity.

Slag penetration

The slag can penetrate through the refractory matrix.
At this stage, slag penetration cannot be directly put in relation to refractory corrosion, but it should be considered part of the global corrosion mechanism since most of the grains reached by the penetrated slag are partially or even totally degraded.
Tab. 5 reports the maximum values of slag penetration depth observed with the three slags. It is expected that the extent of penetration of a slag depends on slag viscosity and interfacial tension between slag and ZrO_2. In this case, the interfacial tension can be considered as a first approximation depending on the characteristics of the slags used, that is on the slag surface tension.
However there is no agreement between slag penetration and calculated [16] slag viscosity and surface tension [17] values reported in Tab. 6. This can be explained by considering that the chemical composition of the penetrated slag can be modified by reactions like decarburation and dissolution of stabilising agent CaO. The reaction with the graphite matrix typically causes a decrease of MnO and SiO_2, the reaction with the ZrO_2 grains typically leads to an increase of CaO that is lost from the grains. This leads to the consideration that slag penetration could depend on characteristics of the modified penetrated slag rather than on the starting slag composition used.

CONCLUSIONS

Zirconia is usually utilised in Submerged Entry Nozzle (SEN) in the slag contact zone, because of its high resistance to corrosion. The occurrence of SEN corrosion is often the phenomenon determining the duration of the casting sequence.
An activity has been carried out to investigate the corrosion mechanism of calcia stabilised zirconia based refractory in presence of slag and steel. Slags with different activity of its constituents have been used.
The carried out activity individuate three main phenomenon operating at the same time:
1. Graphite consumption: the graphite of the refractory may be lost not only by direct dissolution into the steel, but also for the reaction with slag constituents. The reactions between slag components as SiO_2 and MnO that can oxidise the graphite needs the presence of the metallic phase to take place. The higher are the activity values of the above mentioned species the more is the level of decarburization of the refractory. Of course, a higher decarburization level of the refractory implies a higher global corrosion rate.
2. Zirconia grains degradation: this is associated with the dissolution of the stabilising agent CaO. A correlation between the “capacity” of the slag to dissolve CaO and the extent of degradation of the zirconia grains has been found. Slags with high SiO_2 and low CaO activities cause high levels of zirconia grains degradation up to a complete crushing, thus concurring to a faster global corrosion of the material.
3. Slag penetration: the slag penetrates through the refractory matrix. The penetrated slag interacts with the zirconia grains in the inner parts of the refractory beyond the borderline of the decarburised layer. The grains interacted with this penetrated slag are often partially or even totally degraded. This means that also the phenomenon of slag penetration can participate at the global corrosion mechanism. In general, the extent of slag penetration can be put in relation with slag properties like viscosity, but it must be taken into account that the composition of the penetrated slag can vary depending on the reactions involved in the interaction mechanism.
This work demonstrated that the same ZrO_2/C refractory material underwent corrosion with different extents when

	Slag 1	Slag 2	Slag 3
Penetration (μm)	400	400	500

▲
Tab. 5
Depth of slag penetration inside zirconia refractory.
Profondità di penetrazione delle tre scorie nel refrattario.

	Slag 1	Slag 2	Slag 3
Viscosity (Pa·s)	2.2	4.6	1.5
Surface tension (mN/m)	350	362	345

▲
Tab. 6
Calculated viscosity according to Ref. 16 and calculated surface tension according to Ref. 17 for the three slags used in the experimental tests.
Viscosità calcolate usando il modello del rif. 6 e tensioni superficiali calcolate secondo il modello riportato nel rif. 17 per le tre scorie usate nei test sperimentali.

interacting with different slags. The global corrosion of the material is mainly due to the consumption of the graphite matrix and the degradation of the zirconia grains. The increase of the activities of slag components like SiO_2 and MnO that are more aggressive towards the carbonaceous matrix and the subsequent decrease of CaO activity that implies an increase of the capacity of the slag to dissolve CaO, cause a shortening of the refractory lifetime.

In the reality of steel casting where different casting powders can be used, the application of the obtained results can give indications about the increasing or the shortening of the lifetime of the refractory used for SEN.

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ABSTRACT

MECCANISMI DI CORROSIONE DEI REFRATTARI DI ZIRCONIA PER EFFETTO DELL'INTERAZIONE CON LA SCORIA IN PRESENZA DI ACCIAIO

Parole chiave:

I refrattari a base zirconia/carbone spesso sono utilizzati per realizzare quella parte dello scaricatore paniera/lingottiera che è in contatto con la scoria delle polveri di colaggio. Tuttavia è noto dalla esperienza industriale che tali materiali hanno una notevole variabilità di comportamento nei confronti della resistenza alla corrosione a seguito della interazione con la scoria.

Spesso, nella selezione dei materiali più idonei ad essere utilizzati negli scaricatori per la colata continua si segue un approccio empirico, per cui si testano direttamente sul campo diversi refrattari per selezionare, in riferimento al tipo di acciaio e di scoria, quello più resistente.

In letteratura esistono molti studi sui meccanismi di degradazione della zirconia, la maggior parte dei quali basati su meccanismi di tipo "ciclico", in cui l'ossido è attaccato dalla scoria e la grafite, che rimane libera, viene sciolta dall'acciaio. Tuttavia le conclusioni circa gli aspetti controllanti la corrosione di questi materiali sono spesso contraddittori, anche in relazione alle diverse condizioni sperimentali utilizzate per studiare i fenomeni.

In questo articolo sono mostrati i risultati di una specifica attività sperimentale di laboratorio per chiarire meglio il meccanismo di corrosione dei refrattari di zirconia quando interagiscono simultaneamente con la scoria e l'acciaio. I risultati hanno mostrato che oltre alla dissoluzione della zirconia nella scoria e della grafite nell'acciaio, altri fenomeni intervengono contribuendo alla corrosione globale del materiale. Gli esperimenti infatti hanno evidenziato il ruolo importante che svolge l'acciaio nel disciogliere al suo interno i prodotti delle reazioni tra scoria e carbone (ad esempio SiO2+C → SiO+CO ed MnO+C→Mn+CO) spingendo fortemente la reazione verso i prodotti ed accelerando l'attacco della scoria sul carbonio.

In estrema sintesi si può affermare che la corrosione dei materiali a base zirconia e carbone è un fenomeno complesso che è controllato da una serie di parametri tra cui i principali sono l'attività delle specie presenti nella scoria, la porosità del refrattario e le caratteristiche della matrice carboniosa.