Original Article

Densification mechanism of porous alumina plugs by molten steel with different oxygen levels

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ARTICLE INFO

Keywords:

Refractory

Porous alumina

Hydrex probe measurements

Steel

Densification

ABSTRACT

To investigate the densification of porous alumina plugs, hydrogen measurements, using the Hydrex probe system, were performed in molten steel with different oxygen levels at around 1600 °C. The oxygen contents in molten steel were controlled by Al and Fe-Si alloy additions to 664, 296, 92, 51 and 2.5 ppm, respectively. High oxygen levels (> 92 ppm) in molten steel were found to favor the infiltration of steel into porous alumina plug. The infiltrating steel interacts with SiO_2 -containing phases and Al_2O_3 inside the plug, forming liquid $\text{FeO-Al}_2\text{O}_3\text{-SiO}_2$ slag and FeAl_2O_4 (hercynite). These newly formed phases, along with the infiltrating steel fill the porous structure of the alumina plugs. As a result, severe densification was observed inside the alumina plugs in contact with molten steel containing high oxygen levels. In comparison, no densification occurred in the plugs contacting with the steel having low oxygen contents of 51 and 2.5 ppm.

1. Introduction

Porous alumina ceramic has been widely used in primary steel-making (EAF and Converter shop) and ladle metallurgy (RH and Tundish practice) as ceramic bells for hydrogen measurements (Hydrex probe system) [1–3], ceramic filters [4,5] and purging plugs [6,7], owing to its low cost and the high melting point of Al_2O_3 . However, a drawback of using porous alumina ceramics is their vulnerability to steel with high oxygen levels. For example, using the Hydrex system (hydrogen probe), the hydrogen content of liquid steel is measured by means of determining the hydrogen concentration in a nitrogen carrier gas. The carrier gas is injected into the steel through the probe to absorb the hydrogen until equilibrium is attained between gas and steel, and is then recollected by a porous alumina plug and then analyzed in the pneumatic unit (Fig. 1). However, it has been observed that the alumina plug in such measurement suffers from different levels of densification, thereby affecting the recirculation of carrier gas and thus the accuracy of the measured hydrogen concentration. Therefore, knowledge of the densification mechanism of alumina plugs is indispensable in improving the lifetime of porous alumina ceramic and controlling the steel quality and operation safety during ironmaking and steelmaking processes.

Interactions between dense alumina and liquid steel have been reported in a number of studies [8–12]. It is reported that Al_2O_3 is

unwetted by molten steel. However, Al_2O_3 will be wetted by molten steel once the steel is contaminated with oxygen and this wettability is favored by increasing the oxygen level in the steel [8–12]. FeAl_2O_4 hercynite can then be generated at the Al_2O_3 /steel interface by the Al_2O_3 /steel interaction [8–12]. It can be therefore inferred from these results that the densification of porous alumina plug may be caused by the wetting of molten steel with oxygen, which results in the infiltration of molten steel. However, until now there are no experimental studies available confirming this conjecture.

In this work, the densifying behavior of porous alumina ceramic in molten steel is investigated. The tests were carried out by hydrogen probe measurements in molten steel in an induction furnace. To examine the influence of oxygen level on the densification behavior, the oxygen concentration in the steel was controlled by adding different amounts of Fe-Si alloy and Al during the tests. The densification mechanisms are studied by the characterization of the microstructure of the porous alumina ceramics after tests, using scanning electron microscope (SEM) equipped with energy dispersive spectroscopy (EDS).

2. Experimental

2.1. Experiment set-up and procedure

Hydrogen measurements (Hydrex probe system) were conducted in

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Fig. 1. Schematic of the porous alumina plug during hydrogen measurements (Hydrys probe system).

an induction furnace (Inductotherm, Elphiac) at Electro-Nite (Houthalen, Belgium). Approximately 250 kg of steel was held in a refractory crucible, the inner lining of which consists mainly of MgO, and melted at around 1600 °C in the furnace. The schematic drawing of the probe for hydrogen measurement is shown in Fig. 1. A series of hydrogen probe measurements was performed by adding deoxidation agents (Fe-Si alloy and Al) to the molten steel in order to reduce the oxygen content. The first measurement was performed with an initial oxygen level of 664 ppm before the first killing. After each addition of Fe-Si alloy and Al, oxygen in the molten steel was examined by an oxygen probe and a metal sample was taken for compositional analysis with spectroscopic spark emission. After the oxygen content was found to be stable, a new hydrogen probe measurement was performed. The measured oxygen contents and steel composition are listed in Table 1. Curves of hydrogen content and recollected carrier gas pressure were recorded and displayed on the screen of the processor. From these curves one can indirectly observe the densifying extent of the alumina plug during measurements (as discussed in Section 3.2.1). After measuring for around 20s or 60s, depending on the extent of densification, the probe was removed from the molten steel and quenched in a stream of nitrogen.

2.2. Sample analysis technique

After measurements, alumina plugs were recovered for microstructural investigation. To evaluate the interaction between the alumina plug and molten steel, specimens were extracted at the upper part along the vertical direction from each recovered plug as demonstrated in Fig. 2. The specimens were embedded in a low viscosity resin

Fig. 2. Sample extraction scheme for SEM and XRD investigation.

(Epofix) by vacuum impregnation, ground with diamond plates and polished with diamond paste. The polished specimens were coated with a layer of carbon and characterized with a scanning electron microscope (SEM, XL-30 FEG, FEI), equipped with an energy dispersive spectroscope (EDS, EDAX) with an ultra-thin window. The plug surface contacting with molten steel after testing (as shown in Fig. 2) was slightly ground to keep it flat and characterized by X-ray powder diffraction (XRD, D2, Bruker) to examine phase compositions at the steel/plug interface.

2.3. Thermodynamic calculations

The thermodynamic software package FactSage 7.1 was used to support the analysis results [13]. Equilibrium calculations were performed with the equilibrium module EQUILIB, which is based on the minimization of the Gibbs free energy, and the FSstel, FT oxide and Fact PS databases. The following possible solution phases were chosen in the calculations: (1) FSstel-LIQU, (2) FToxide-SLAGA (molten oxide phase); (3) FT oxide-MeO_A (oxide solid solution); (4) FT oxide-SPINA (spinel solid solution); (5) FToxide-Mull (mullite solid solution); (6) FT oxide-CORU (corundum), and (7) FACT PS (gas phase). The steel/refractory interactions were modeled at 1600 °C by addition of one gram or two grams (x g) refractory components of Al₂O₃, mullite (71.8 wt% Al₂O₃ and 28.2 wt% SiO₂) or a SiO₂-Al₂O₃ mixture (50 wt% Al₂O₃ and 50 wt% SiO₂) to the steel [(100-x-y-z) g] without or with 0.47wt% Si (y g). SiO₂-Al₂O₃ mixture was used to mimic the SiO₂-rich phases in the plug. The oxygen level in the molten steel ranges from 0 to 700 ppm (z g) in the calculation.

3. Results

3.1. As-delivered porous alumina plug

Fig. 3 presents the microstructure of the as-delivered alumina plug.

Table 1

Experimental parameters for the hydrogen probe measurements.

Exp. no.	Temperature (°C)	Q (ppm)	Chemical composition of the steel (wt%)					
			C	Si	Ni	Cu	Fe	Others
1	1608	664	0.03	0.01	0.23	0.45	98.8	0.48
2	1626	296	0.03	0.09	0.23	0.45	98.7	0.50
3	1627	92	0.03	0.21	0.23	0.45	98.5	0.58
4	1616	51	0.03	0.31	0.22	0.45	98.3	0.49
5	1627	2.5	0.02	0.47	0.23	0.45	98.4	0.43

Fig. 3. (a) overview of the as-delivered alumina plug, (b) and (c) detailed images of selected areas X and Y, respectively, and (d) Al and (e) Si EDS elemental mapping of the select area Y; A = Al_2O_3 phase; SA = SiO_2 -containing phase; P = pores.

A very extensive open pore network is observed, since the plug is porous. Solid phases, mainly consisting of pure Al_2O_3 , form a framework in the plug. Besides the pure alumina phase, SiO_2 -containing phases ('SA' in Fig. 3b and c) are found mainly located at the grain boundaries of Al_2O_3 phases as impurities. A mixture of Al-poor and SiO_2 -rich phases, as shown in Fig. 3c–e, is observed. Compositional analyses by EDS that the Al_2O_3 -poor phase would be crystal mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) containing $65.4 \pm 1.5 \text{ mol}\%$ Al_2O_3 and $34.5 \pm 1.4 \text{ mol}\%$ SiO_2 , and the SiO_2 -rich phase would be an amorphous phases consisting of $28.3 \pm 14.6 \text{ mol}\%$ Al_2O_3 , $68.9 \pm 13.5 \text{ mol}\%$ SiO_2 , $2.5 \pm 1.0 \text{ mol}\%$ Na_2O , and $0.3 \pm 0.2 \text{ mol}\%$ CaO .

3.2. Macroscopical observation of the densification behavior

3.2.1. Measured curves of recollected gas pressure and hydrogen content

Fig. 4 shows the measured curves of hydrogen content and recollected carrier gas pressure. In Fig. 4, the O level (Q in the figure), which decreases from 664 ppm to 2.5 ppm, is the main parameter. As demonstrated in Fig. 4a and b, the pressure of the carrier gas (recirculated in the system) abruptly dropped to an extremely low value of below 200 hPa and the hydrogen contents sharply increased after measuring for between 10 s and 20 s. These observations indicate that serious densification of alumina plugs occurred in Test 1 and Test 2, in which the steel contained 664 ppm and 296 ppm oxygen, respectively. When the oxygen content was lowered to 92 ppm in Test 3 (Fig. 4c), the

decrease in the carrier gas pressure and increase of the hydrogen content during the measurement was moderated, suggesting that the extent of densification was reduced compared with Test 1 and Test 2. However, the amount of carrier gas, which was recollected by the alumina plug, was still insufficient for the measurement. With further decreasing the oxygen level in the molten steel to 51 ppm and 2.5 ppm in Test 4 (Fig. 4d) and Test 5 (Fig. 4e), respectively, the hydrogen concentrations in the carrier gas gradually increased to a maximum value of 7.0 ppm after measuring for 50 s and stabilized thereafter. Meanwhile, the pressure of carrier gas decreased slowly and kept constant after measuring for 50 s. These characteristics of the measured curves suggest that there was no alumina plug densification in Test 4 and Test 5. It is obvious from the measured curves that the densification of alumina plugs is related to the oxygen level in the molten steel.

3.2.2. Appearance of the tested alumina plug

The appearances of recovered alumina plugs after completion of the tests are shown in Fig. 5. The amount of steel adhered on the outer surface of alumina plug is closely correlated with the oxygen content in the molten steel. A substantial quantity of attached steel was observed for Test 1 and 2 with oxygen contents of 664 and 296 ppm, respectively. With decreasing the oxygen contents to 92 ppm (Test 3), 51 ppm (Test 4) and 2.5 ppm (Test 5), the amount of attached steel continuously decreased. These observations indicate that higher oxygen levels in the molten steel favoured the sticking of steel on the alumina plug surface.

Fig. 4. The measurement curves of the hydrogen content and those of carrier gas pressure: (a) Test 1 $\underline{Q} = 664$ ppm, (b) Test 2 $\underline{Q} = 296$ ppm, (c) Test 3 $\underline{Q} = 92$ ppm, (d) Test 4 $\underline{Q} = 51$ ppm, and (e) Test 5 $\underline{Q} = 2.5$ ppm.

This is consistent with the results shown in Fig. 4, where the higher oxygen level in the steel brought about a more severe densification of the alumina plug. To understand the influence of oxygen content in liquid steel on the densification of alumina plugs, the microstructure of tested alumina plugs was analyzed and is presented in the next section.

3.3. Microstructural features of tested alumina plugs

Phase compositions at the steel/plug interface from Test 2 (with 296 ppm oxygen) are shown in Fig. 6. α - Al_2O_3 , metallic iron, Fe_2SiO_4 fayalite, FeAl_2O_4 hercynite, $\text{Fe}_{2.932}\text{O}_4$ magnetite and Fe_2O_3 hematite are observed at the plug surface contacting with the molten steel. FeAl_2O_4

Fig. 5. Appearance of the alumina plugs after testing in the molten steel with distinct oxygen levels from Test 1 to Test 5.

Fig. 6. Phase composition at liquid steel/plug interface of the sample from Test 2. The FeAl_2O_4 hercynite (spinel) is identified by comparing the peak positions in this particular work with those in Ref. [14,15].

hercynite ($2\theta = 36.4$) and Fe_2SiO_4 fayalite are most likely generated from the interactions between molten steel and plug. $\alpha\text{-Al}_2\text{O}_3$ and metallic iron are from the plug and molten steel, respectively. $\text{Fe}_{2.932}\text{O}_4$ magnetite and Fe_2O_3 hematite are possibly formed by the oxidation of attached steel after probe testing.

An overview of the microstructure of the recovered alumina plug from Test 1 (with 664 ppm oxygen) at the molten steel/ Al_2O_3 plug interface is shown in Fig. 7a. A completely different microstructure as compared with the virgin sample (Fig. 3) is observed. At the hot face of the alumina plug an interaction layer with a thickness of over 3 mm was seen. This layer consists of a large amount of infiltrating steel, unreacted alumina particles, and newly-formed $\text{FeO}_n\text{-Al}_2\text{O}_3\text{-SiO}_2$ liquid slag, hercynite (FeAl_2O_4) and fayalite (Fe_2SiO_4), as indicated by XRD

(Fig. 6) and EDS (Table 2) measurements. In the interaction layer, FeAl_2O_4 is observed in the $\text{FeO}_n\text{-Al}_2\text{O}_3\text{-SiO}_2$ slag matrix which surrounds undissolved alumina grains. The original open pore network in the plug was densified with the infiltrating steel and newly-formed phases from the interactions between the steel and the plug (Fig. 7c, d).

3.4. Influence of oxygen content on the steel infiltration

Fig. 8 shows the changes in the amounts of the infiltrating steel and the newly-formed phases (hercynite, fayalite and $\text{FeO}_n\text{-Al}_2\text{O}_3\text{-SiO}_2$ liquid slag) in the interaction layer at the surface of the samples contacting with molten steel as a function of oxygen content in the molten steel bath. The thickness of the infiltrated layer continuously decreases from > 3 mm in Test 1 with an oxygen level of 664 ppm (Fig. 7a), to 1.6 mm in Test 3 (Fig. 8a) and 200 μm in Test 5 (Fig. 8b) with oxygen contents of 92 ppm and 2.5 ppm, respectively. It is evident that the amount of infiltrating steel decreases with lowering the oxygen content in the steel bath. Correspondingly, the amount of the newly formed hercynite, fayalite and $\text{FeO}_n\text{-Al}_2\text{O}_3\text{-SiO}_2$ liquid slag at the surface of alumina plugs is also found to be decreased with reducing the oxygen content in the steel bath. When the steel was killed to 2.5 ppm oxygen (Test 5, Fig. 8b), only a very small amount of steel was found in the pores of Al_2O_3 plug at the steel/plug interface. Compared with the sample from Test 1 with an oxygen content of 664 ppm (Fig. 7a), no distinct interaction layer was observed at the surface of the sample from Test 5 (Fig. 8b). This is compatible with the visual observations in Fig. 5 and with the hydrogen measurement results (Fig. 4).

4. Discussion

4.1. Densification mechanism of porous alumina plugs

Based on the aforementioned results, it can be summarized that the

Fig. 7. Microstructure at liquid steel/ plug interface of the sample from Test 1: (a) overview of the interaction layer, and (b), (c) and (d) enlarged views of positions X, Y, and Z in (a), respectively: Me = metallic iron particle; A = Al_2O_3 ; L = $\text{FeO}_n\text{-Al}_2\text{O}_3\text{-SiO}_2$ liquid slag; H = FeAl_2O_4 hercynite; Fa = Fe_2SiO_4 fayalite; $\times$ = analysis spots (the chemical compositions are listed in Table 2).

Table 2

Chemical compositions of the selected points in the interaction layer in Fig. 6, as determined by SEM-EDS.

Spot No.	Phase	FeO wt% [mol%]	Al ₂ O ₃ wt% [mol%]	SiO ₂ wt% [mol%]	MgO wt% [mol%]	Cr ₂ O ₃ wt% [mol%]	MnO wt% [mol%]
1	Hercynite	31.8 [37.9]	52.1 [43.8]	–	4.9 [10.4]	8.7 [4.9]	2.5 [3.0]
2	Fayalite	62.3 [58.3]	1.3 [0.9]	30.4 [33.6]	1.2 [2.0]	–	4.7 [4.5]
3	FeO _n -Al ₂ O ₃ -SiO ₂ liquid slag	31.3 [29.9]	18.1 [12.2]	45.7 [52.2]	1.2 [2.0]	–	3.7 [3.6]
4	Hercynite	33.8 [40.3]	59.6 [50.0]	–	3.2 [6.7]	1.7 [1.0]	1.7 [2.1]

(a) Test 3, $\underline{Q}$ = 92 ppm **(b) Test 5, $\underline{Q}$ = 2.5 ppm** **Fig. 8.** Changes in the amount and depth of steel infiltration at the hot face of the samples from (a) Test 3, $\underline{Q}$ = 92 ppm; and (b) Test 5, $\underline{Q}$ = 2.5 ppm, showing the influence of oxygen level on the steel infiltration: Me = metallic iron particle; A = Al₂O₃; H + L = FeAl₂O₄ hercynite + FeO_n-Al₂O₃-SiO₂ liquid slag. Dash line in the figure shows the infiltration limit of molten steel.

densified porous alumina plugs are caused by the infiltration of steel into the plug and by the steel/Al₂O₃ plug interactions to form liquid FeO_n-Al₂O₃-SiO₂ slag, FeAl₂O₄ hercynite and fayalite in the plug. As shown in Fig. 7, the infiltrating steel and the newly formed phases filled the porous structure of the alumina plug, thereby blocking the path for the carrier gas recirculation (Fig. 4).

4.1.1. Infiltration of molten steel in porous alumina plugs

The presence of oxygen in molten steel and oxygen from the carrier nitrogen gas and porosities in plugs bring about a shift from non-wetting to wetting behavior in the iron/alumina system. The contact angle between molten steel and Al₂O₃ decreases with increasing oxygen contents in the steel [8–12]. For instance, the measured contact angles between liquid iron and Al₂O₃ are 132°, 71° and 68° corresponding oxygen partial pressures of 1×10^{-14} , 9.9×10^{-4} and 3.0×10^{-3} , respectively [8]. Considering that the same quality of carrier nitrogen gas and porous Al₂O₃ plug were used in the probe measurements, oxygen supplied from the carrier gas and plugs in different tests should be also the same. Therefore, it can be concluded that the infiltration of molten steel in the alumina plugs is favored by a high oxygen level in the steel (Fig. 8a), whereas the infiltration of steel into the alumina plug was limited in the steel with a low oxygen content (Fig. 8b).

4.1.2. Interaction mechanisms between infiltrating iron and alumina plugs

Note in Figs. 6 and 7 that a large amount of FeO_n-Al₂O₃-SiO₂ slag, FeAl₂O₄ hercynite and Fe₂SiO₄ fayalite are observed when the alumina plug was infiltrated by molten steel, whereas a low level of FeO-bearing phases is found in the plug contacting with molten steel having a low oxygen level (Fig. 8b). Phase diagram analyses of the FeO_n-Al₂O₃-SiO₂ ternary system (Fig. 9) illustrate that liquid FeO_n-Al₂O₃-SiO₂ slag and FeAl₂O₄ hercynite are stable phases at the testing temperatures (~1600 °C) from the steel/plug interactions. Al₂O₃ and SiO₂ in the slag are mainly from the alumina plug, and FeO was formed by the oxidation of liquid steel. FeAl₂O₄ hercynite precipitates from the slag/plug interactions once the slag is (locally) saturated with Al₂O₃. The observed Fe₂SiO₄ fayalite should precipitate during quenching of the plug after testing.

Thermodynamic calculations, as shown in Fig. 10, illustrate that FeO_n-Al₂O₃-SiO₂ slag is generated by adding two grams of mullite (3Al₂O₃·2SiO₂) into the steel at 1600 °C, whereas no slag is generated with the addition of Al₂O₃. As shown in Fig. 10a, the increase of oxygen

content from 0 ppm to 700 ppm in the steel only slightly increases the amount of the slag (from 1.368 g to 1.372 g) with the addition of two grams of SiO₂-Al₂O₃ mixture. These results imply that FeO is mainly formed through the redox-reactions between steel (Fe) and SiO₂ from SiO₂-containing phases in the plug. Such oxidation of Fe by SiO₂ from SiO₂-containing refractories or mold flux has been also reported [19,20]. Note in Fig. 10a that compared with the addition of two grams of mullite, a greater amount of slag is generated when one or two grams SiO₂-Al₂O₃ mixture is/are added into the steel because of the enhanced oxidation of molten steel, indicating that the presence of SiO₂-rich phases in the porous plug favors the generation of FeO_n-Al₂O₃-SiO₂ slag. Additionally, oxygen from the carrier nitrogen gas, and air and/or moisture in the porosities of the porous alumina plug, can also promote the oxidation of molten steel and facilitates the slag formation. Along with the molten steel, this liquid slag also infiltrated into the porous alumina plug, along the open pore network and grain boundaries (Figs. 6 and 7). Since the increased oxygen content in the molten steel favors the infiltration of steel into the porous alumina plug, more SiO₂-containing phases inside the plug could contact with molten steel. As a result, larger amounts of FeO_n-Al₂O₃-SiO₂ slag are generated in the plug contacting with molten steel having higher oxygen levels. In comparison, a small amount of steel infiltrated into the porous alumina plug in the molten steel with a low oxygen content (2.5 ppm, Fig. 8b). As a result, the formation of FeO_n-Al₂O₃-SiO₂ liquidus slag is suppressed. Additionally, the increased Si content in molten steel, due to the addition of Fe-Si alloy, also hinders the generation of liquidus slag by suppressing the redox-reactions between steel (Fe) and SiO₂ (Fig. 10).

To describe plug components dissolution, and plug/steel (or slag) interactions during testing and precipitates formation during quenching in local regions at plug/steel (or slag) interface in the plug, the phase diagram of FeO_n-Al₂O₃-SiO₂ ternary system, representing the equilibrium state, can be used. As shown in Fig. 9, the initially formed FeO_n-Al₂O₃-SiO₂ slag is completely undersaturated in both Al₂O₃ and SiO₂, as a result Al₂O₃ and SiO₂-containing phases in the porous alumina plug inevitably dissolved into the slag. The evolution of the slag composition during the dissolution of plug components follows an idealized path from point “a” with a high FeO_n content to point “b” (or point “b’”) and then to point “c” as described in Fig. 9, depending on the dissolution rates and amounts of Al₂O₃ and SiO₂-containing phases into the slag. Besides the dissolution of Al₂O₃ and SiO₂, CaO and Na₂O in the plug can also dissolve into the liquid FeO_n-Al₂O₃-SiO₂ slag. Additionally, other

Fig. 9. Liquidus projection at 1600 °C in the $\text{Al}_2\text{O}_3\text{-FeO}_x\text{-SiO}_2$ in contact with metallic iron after Schairer [16] and Galakhov [17], as drawn by Muan and Osbon [18].

steel components, e.g. Mn, could also be oxidized into MnO [21] and enter into the liquid slag. The presence of these oxides, e.g. CaO , Na_2O and MnO , in the slag could further decrease the slag melting temperature and thus favor the Al_2O_3 and SiO_2 dissolution, thereby increasing the amount of liquid slag. When slag composition reaches point “c”, the slag will be saturated with FeAl_2O_4 hercynite. The FeAl_2O_4 hercynite, therefore, precipitated from the slag at the slag/ Al_2O_3 interface (Fig. 7a) according to Eq. (1).

Oxides, e.g. MgO , MnO and Cr_2O_3 originating from refractory dissolution or from steel oxidation, in the slag would be incorporated in the hercynite formation, generating hercynite-based solid solutions (Table 2).

Further generation of FeO_x at the steel/plug interfaces and dissolution of Al_2O_3 into the slag could enhance the formation of hercynite along the unreacted Al_2O_3 grains [22]. The liquid slag composition, therefore, changes to point “d” (in Fig. 9). When the plug was cooled down after the measurement, hercynite would further precipitate from the slag and might exhibit dendritic and angular shaped morphology, as shown in Fig. 7d. Fayalite phase can also precipitate from the SiO_2 -rich slag with further cooling of the plug, which could be proved by its dendritic and angular shape (Fig. 7b). As the precipitation of hercynite and fayalite would enrich the liquid slag in SiO_2 , the slag composition changes to point “e” in Fig. 9. This is in good agreement with the

chemical composition at spot 3 (Table 2).

4.1.3. Densification scheme of porous alumina plugs

Based on the microstructural and chemical analyses of the recovered alumina plugs, a scheme of the densified porous alumina plug in molten steel with oxygen contamination is proposed in Fig. 11. The infiltration of high oxygen content molten steel and formation of $\text{FeO}_x\text{-Al}_2\text{O}_3\text{-SiO}_2$ slag due to redox-reactions between steel (Fe) and SiO_2 from SiO_2 -containing phases in the plug are primarily responsible for the densification of the plug. The high oxygen level in the steel favors the steel infiltration by improving the wetting of Fe on Al_2O_3 . As a result more SiO_2 -containing phases interact with molten steel, generating larger amounts of $\text{FeO}_x\text{-Al}_2\text{O}_3\text{-SiO}_2$ slag inside the porous alumina plug (Fig. 11a). The newly-formed liquid $\text{FeO}_x\text{-Al}_2\text{O}_3\text{-SiO}_2$ slag and the infiltrating molten steel fill the open pore network of the plug (Fig. 11b). FeAl_2O_4 hercynite is generated from the steel/plug interactions once the slag is (locally) saturated with Al_2O_3 (Fig. 11b). As a result, the microstructure at the hot face of the alumina plug changed from the original porous structure with a large open pore network (Fig. 3a) to a dense mixture consisting of infiltrating steel, hercynite, liquid slag and unreacted Al_2O_3 particles (Figs. 7 and 11c), thereby blocking the carrier gas recirculation. The densification of the porous alumina plug is therefore occurring.

To decrease the densification and thereby to increase the accuracy of the hydrogen measurement, measures can be suggested as

Fig. 10. (a) amounts of $\text{FeO}_x\text{-Al}_2\text{O}_3\text{-SiO}_2$ liquidus slag generated by adding refractory components into molten steel, and (b) slag compositions $\text{FeO}_x\text{-Al}_2\text{O}_3\text{-SiO}_2$ liquidus slag generated in molten steel without or with 0.47 wt% Si, as predicted by thermodynamic calculations at 1600 °C: GP, $\text{SiO}_2\text{-Al}_2\text{O}_3$ mixture, Mu, mullite.

Fig. 11. Schematic representation of the densification of porous alumina plug in molten steel.

followings: (1) preventing iron infiltration into the plug, by reducing the dimension of the open pores or by using other plug materials, which are less wetted by iron with a high oxygen level; and (2) mitigating liquid slag formation in the interaction layer by reducing or avoiding the SiO_2 in the plug.

5. Conclusions

The densifying behavior of the porous alumina plug was investigated by hydrogen measurement (Hydrys probe system) tests. These tests were performed in an induction furnace filled with steel with distinct oxygen levels of the molten steel controlled by Fe-Si alloy and Al killing. Based on macroscopical observations and microstructural characterization of the recovered alumina plug, the following conclusions can be drawn:

- (1) The densifying behavior of the alumina plug was significantly affected by the oxygen content in molten steel, as demonstrated by the measured curves of the hydrogen content and carrier gas pressure, and by the appearance of the plug after measurements. The higher the oxygen level in the steel, the more severe densification of the alumina plug is.
- (2) $\text{FeO}_n\text{-Al}_2\text{O}_3\text{-SiO}_2$ liquidus slag was generated due to the redox-reactions between steel (Fe) and SiO_2 from SiO_2 -containing phases in the plug.
- (3) Oxygen containing steel infiltrated into the porous alumina plug, because oxygen can favor the wetting of iron on Al_2O_3 . The enhanced molten steel infiltration favors the generation of $\text{FeO}_n\text{-Al}_2\text{O}_3\text{-SiO}_2$ liquidus slag. FeAl_2O_4 -based hercynite precipitated along unreacted Al_2O_3 phase from the slag once the slag is (locally) saturated with Al_2O_3 . The infiltrating steel, the newly-formed slag and hercynite fill the open pore network of the plug, thereby blocking the path for the carrier gas recirculation and thus densifying alumina plugs. Therefore, the densification of alumina plug occurs in molten steel with high oxygen levels.
- (4) High SiO_2 content phases in the plug facilitate the formation of liquid $\text{FeO}_n\text{-Al}_2\text{O}_3\text{-SiO}_2$ slag, favoring the densification of alumina plug.
- (5) The densification of porous alumina plug was limited by lowering the oxygen level in molten iron. This is because the infiltration of steel was hindered and the formation of $\text{FeO}_n\text{-Al}_2\text{O}_3\text{-SiO}_2$ slag was

inhibited.

Acknowledgements

The authors are grateful to the engineers of Electro-Nite for their close co-operation.

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