Interaction between Steel and Distinct Gunning Materials in the Tundish

Pengcheng YAN,1) Marie-Aline Van ENDE,2) Enno ZINNGREBE,3) Sieger van der LAAN,3) Bart BLANPAIN1) and Muxing GUO1)*

1) Department of Materials Engineering, KU Leuven, Kasteelpark Arenberg 44 - Bus 2450, BE-3001 Leuven, Belgium.
2) Department of Mining and Materials Engineering, McGill University, 3610 University Street, Montreal, QC, H3A 0C5 Canada.
3) Tata Steel Europe, Research Development and Technology, Ceramic Research Center, PO Box 10000, 1970 CA IJmuiden, The Netherlands.

(Received on March 8, 2014; accepted on July 23, 2014)

Gunning materials are used as a dispensable protective layer to extend the tundish life. Their use however, affects the steel cleanliness by introducing steel reoxidation and exogenous inclusions. In the present work, the interaction between molten steel and three types of refractory, i.e. MgO, Al2O3, and MgO + 2MgO·SiO2 based gunning materials (GM) have been investigated. Compared to MgO and MgO + 2MgO·SiO2 GM, the Al2O3 GM exhibited better infiltration resistance to molten steel. The two phase MgO + 2MgO·SiO2 GM was found to be less prone to steel infiltration than single-phase MgO GM. The compositional evolution of steel influenced by gunning material was experimentally measured and also predicted with thermodynamic equilibrium calculations. The steel cleanliness in terms of inclusion size, number density, area fraction and morphology was measured and evaluated. Although large Al2O3/AlTiOX inclusions were formed through the erosion of Al2O3 GM, the use of Al2O3 GM resulted in an improved steel cleanliness due to its lower content of reducible compounds compared to that of MgO and MgO + 2MgO·SiO2 GM.

KEY WORDS: steel/refractory interaction; tundish; inclusions; gunning materials.

1. Introduction

Interactions between steel and refractory materials are of fundamental importance for steelmaking industry. Most of the process steps in steelmaking involve such interactions,1,2) but their nature and characteristics are as variable as the compositions of both molten steel and refractory materials.3–6) The investigation of such interaction is a longstanding topic of experimental and analytical studies. Most work on such interaction and its influence on steel cleanliness concentrate on the main types of refractory which have a prolonged exposure time to molten steel in integrated steelmaking vessels,1–6) such as for the converter or ladle bricks. There are also a large number of specialized refractory materials that come into contact with molten steels at more distinct handling steps, e.g., tundish and glazed refractories.7–9) Due to its final contact with the molten steel during refining process and its impurity content, tundish refractory is considered as a potential source of steel contamination.3,10) Several groups3,1,6) have confirmed that the presence of FeO contributes to steel reoxidation and results in steel contamination by introducing exogenous inclusions. Lehmann et al. found that SiO2 in tundish refractory can also lead to steel reoxidation, during which two layers, a first solid spinel layer covering on refractory and a second calcium aluminate layer covering the first layer, form at the steel/refractory interface.11) Simões et al. investigated the influence of SiO2 content in refractory on steel cleanliness of an Al killed steel, they concluded that a high SiO2 content in refractory induced a number of large inclusions in steel due to reoxidation reactions, meanwhile large particles can also be brought into steel by erosion of the tundish refractory.6) MgO based refractory performs a good erosion resistance to liquid melts;2) it however leads to the formation of MgO–Al2O3 (MA) spinel inclusions. The refractory component MgO is found to be reduced by carbon at high temperature, and the resulting Mg vapour reacts with the original Al2O3 inclusions in steel to form MA spinel.1,6) In order to improve the wear resistance of tundish refractory and to decrease steel reoxidation, gunning materials (GM) are commonly used in the tundish as a dispensable protective layer between the main tundish refractory and the steel volume. Although gunning material is in contact with steel for a short time, it affects the steel cleanliness due to its direct contact with molten steel at the end of the refining stage. For instance, Mantovani et al. investigated the interaction between MgO based gunning materials and an Al killed steel with respect to steel cleanliness.10) They identified three major interactions at the refractory/steel interface, i.e. steel infiltration into gunning material, formation of an oxidised layer and formation of many particles in the steel near to the steel/refractory interface.10) They also found that the 2MgO·SiO2 in gunning material reacted with the dis-
solved Al in molten steel to form a spinel layer at the interface. Literatures focusing on quantitative investigations on the interaction mechanisms and on the resulting steel cleanliness, which are essential for the gunning material selection and steel quality, however are limited.

In this paper, three types of refractory, viz. MgO, Al₂O₃ and MgO + 2MgO·SiO₂ based gunning materials were tested. Our interest lies in the description of interaction mechanisms on the mineralogical and phase chemical level, which is a necessary prerequisite to understand the influence of the gunning material (both composition and structure) on this steel/refractory interaction. To develop a fundamentally correct characterisation of the interactions, experiments need to be carried out under well-defined chemical conditions, and the phase makeup of the reaction partners has to be adequately determined during successive stages of the interaction. With this in mind, we have developed an appropriate experimental method which is based on a modified atmosphere gas mixing furnace, imposing a fixed oxygen partial pressure throughout the experiment. For the interaction couple, the exposed refractory (the gunning material) is shaped as a container cup in which the molten steel is held. In such way, the steel contacts no other material during the experiment than the defined atmosphere and the refractory of interest. The interactions between the steel/refractory, including chemical reactions, steel infiltration and refractory corrosion were investigated. The influence of gunning material on inclusion characteristics (e.g. inclusion size, number density, morphology and chemistry) was studied as well. This work is designed to provide fundamental knowledge for gunning material selection and steel quality control.

2. Experimental

The experimental set-up and procedure are schematically shown in Fig. 1. An alumina crucible was coated with a layer of gunning material and brought into contact for 2 hours with a Ti-Stabilized Ultra Low Carbon steel (TiSULC, Table 1) under Ar/CO controlled atmosphere. Three tests were performed with different gunning materials viz. MgO, Al₂O₃ and MgO + 2MgO·SiO₂ (Table 2). Around 220 g of steel was charged into the crucible and melted in a vertical tube furnace (Gero, HTRV, MoSi₂ heating elements) at 1550°C. A gas mixture of 10Ar-1CO was blown into the furnace with a flow rate of 7.3 × 10⁻⁶ m³/s and the oxygen partial pressure was measured with a solid state ceramic oxygen sensor (Rapidox 2100), yielding a typical value of about 1 × 10⁻¹⁶ atm at 1550°C. Three steel samples were taken during the test. The first one was obtained just after melting, while the second and third ones were taken after around 30 and 60 or 90 minutes of interaction, respectively. The sampling was achieved by dipping fine Al₂O₃ tubes into the steel. A small volume of steel (around 5 g) was sucked into the alumina tube where it solidified. The tube was subsequently withdrawn to the (cold) top part of the furnace. After 2 hours of interaction, the crucible was lifted into the cold area of the furnace for a relatively rapid cooling, using the hook system attached to the crucible. After completion of the experiment, the furnace was rinsed with Ar to remove the remaining CO. The crucible and the steel samples were then taken out of the furnace for further processing.

The tested gunned crucibles (upper part of Fig. 2) were recovered and subjected to microstructural analysis. The steel/refractory interface was investigated in order to understand the mechanisms of steel/refractory interaction. The polished specimens were assessed with a JEOL 733 EPMA-EDS system, using a semi-quantitative analysis procedure. The obtained steel sample (lower part of Fig. 2) was cut into two parts. The first part of the sample was prepared for inclusions characterisation with Automated Image Analysis (AIA). Cross sections of the steel area were investigated.

<table>
<thead>
<tr>
<th>Test No.</th>
<th>Type</th>
<th>CaO</th>
<th>MgO</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>FeO</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>MgO</td>
<td>4</td>
<td>76</td>
<td>10</td>
<td>–</td>
<td>6</td>
</tr>
<tr>
<td>II</td>
<td>Al₂O₃</td>
<td>1.3</td>
<td>–</td>
<td>3.3</td>
<td>93</td>
<td>2</td>
</tr>
<tr>
<td>III</td>
<td>MgO+M₂S</td>
<td>2</td>
<td>64</td>
<td>25</td>
<td>–</td>
<td>4</td>
</tr>
</tbody>
</table>

M₂S represents 2MgO·SiO₂

![Fig. 1](image_url)
with Scanning Electron Microscope (SEM) coupled with an EDAX-EDS spectrometer and measured with AIA.\textsuperscript{11} The maximum working magnification for the AIA was set to 1000 and the effective minimum detectable area was about 0.5 $\mu$m$^2$. At least 1000 inclusions and 5 mm$^2$ of steel matrix were analysed to evaluate inclusion number, size and composition. The second part of steel sample was used for the inclusion morphology and steel composition assessment. Around 0.3 g steel sample was dissolved in HCl acid solution (1:1) at 80°C, the non-dissolvable inclusions were collected on a membrane filter (0.25 $\mu$m) and subjected for SEM observation. The filtered solution was prepared for steel composition analysis with an inductively coupled plasma atomic emission spectroscopy (ICP-AES, Varian Liberty series II instrument with an axial plasma configuration).

3. Results and Discussion

3.1. Steel/refractory Interaction

3.1.1. Observation at the Steel/refractory Interface

The microstructure of the steel/refractory interface was analysed with EPMA and shown in Figs. 3–5. Three major phenomena can be identified: (1) steel infiltration, molten steel infiltrates into the gunning material (Figs. 3(a), 3(c) and 4(a)); (2) refractory erosion, large inclusions with similar structure and composition as gunning material are found in the steel phase, close to the steel/refractory interface (Figs. 3(b) and 4(b)); and (3) steel reoxidation, an FeOx layer with a thickness of 5–30 $\mu$m forms at the steel/refractory interface (Fig. 5). Figure 3 shows the comparison of the steel infiltration into the refractory for the distinct gunning materials. The extent of infiltration depends on the refractory type and decreases as follows: (a) Test I (MgO, ‘severe’) > (c) Test III (MgO + M\textsubscript{2}S, ‘moderate’) > (b) Test II (Al\textsubscript{2}O\textsubscript{3}, no infiltration). Two-phase refractory system (Fig. 3(c): MgO + M\textsubscript{2}S GM) is less prone to steel infiltration than single-phase refractory (Fig. 3(a): MgO GM).\textsuperscript{12–15} This is because the dihedral angels ($\phi$) between like grains (e.g. signal phase...
refractory) are considerably smaller than that between unlike grains (e.g. two phase refractory). The dihedral angle is a measure of the ability of liquid to penetrate between solid grains: no penetration occurs when $\phi$ is larger than 120°; strong infiltration in case of low $\phi$ ($< 60^\circ$); and complete penetration in case of $\phi$ is zero. For instance, White and Stephenson also found that the steel infiltration between unlike grains was less than between like grains. $\text{Al}_2\text{O}_3$ GM exhibits an excellent infiltration resistance (Fig. 3(b)).

Figure 4 shows the effect of the refractory/steel contact nature on the interactions at the interface. Good wetting between $\text{MgO}$ and steel at the interface (Fig. 4(a), $\theta_{\text{MgO/Fe}} = 78-113^\circ$) results in severe steel infiltration, while $\text{Al}_2\text{O}_3$ GM behaves excellent infiltration resistance to steel due to the poor wetting (Fig. 4(b), $\theta_{\text{Al}_2\text{O}_3/\text{Fe}} > 140^\circ$) between $\text{Al}_2\text{O}_3$ and steel. Since the strongest bonding of the refractory grains (at the refractory/steel interface) with the refractory matrix occurs in the case of minimal wetting between the refractory and liquid metal, $\text{Al}_2\text{O}_3$ GM would be expected to be more resistant to erosion compared to the $\text{MgO}$ GM. However, a large number of alumina grains are found in the steel phase in case of using $\text{Al}_2\text{O}_3$ GM (Fig. 4(b)). This is probably related to the porous microstructure of $\text{Al}_2\text{O}_3$ GM structure, which allows $\text{Al}_2\text{O}_3$ grains to be more easily removed, leading to steel contamination.

The formation of a reaction layer is observed at the steel/refractory interface for all three tests. According to composition analysis with EPMA, this layer consists of $\text{FeO}_x$. A possible mechanism for the $\text{FeO}_x$ layer formation is proposed in Fig. 5, where the formation of the $\text{FeO}_x$ layer is due to the large difference of oxygen potential between refractory and steel phase. Because of the low $P_\text{O}_2$ in the furnace atmosphere (around 10^{-16} atm) and the dissolved Al and Ti, the molten steel has a low content of dissolved oxygen. On the other hand, the refractory can be considered as a potential oxygen provider. The air trapped in pores and the reducible compounds, such as $\text{FeO}$ and $\text{SiO}_2$, may provide oxygen. The lack of oxygen in the metal phase creates a driving force for the oxygen transfer from the refractory, i.e. through the reduction of $\text{FeO}$ and/or $\text{SiO}_2$ to the steel phase. At the refractory/metal interface, the steel meets a large source of oxygen, forming an $\text{FeO}_x$ layer. In contact with $\text{MgO}$ grains, $\text{Fe}^{2+}$ ions from this layer diffuse into the $\text{MgO}$ grain and form a (Mg,Fe)O solid solution. This (Mg,Fe)O solid solution was confirmed with the EPMA analysis. Although $\text{FeO}_x$ layer is observed in all three tests, relatively thicker layer is formed in case of using $\text{MgO}$ based GM ($\text{MgO}$ and $\text{MgO}+\text{TiS}$ GM) compared to the $\text{Al}_2\text{O}_3$ based GM, indicating more oxygen is supplied from $\text{MgO}$ based gunning materials to metal phase.

3.1.2. Compositional Evolution of Molten Steel

The observed result at the steel/refractory interface shows that steel reoxidation occurs when it is in contact with the gunning material (see Fig. 5). This is further confirmed by the compositional evolution of molten steel as shown in Fig. 6. [Al] content rapidly drops to the level of several ppm and a large [Si] pick-up is simultaneously observed in the beginning of all the tests. Thereafter a considerable decrease of [Ti] accompanied with a slight drop of [Mn] is observed in Test I (using $\text{MgO}$ GM), while their contents keep stable in Test II by using $\text{Al}_2\text{O}_3$ GM. As the reaction proceeded, the [Si] starts decreasing in Test I, while it continuously increases in Test II. The compositional evolution of steel implies that (1) $\text{SiO}_2$ in refractory is reduced by the dissolved Al and Ti in molten steel, leading to steel reoxidation; (2) with the further interaction, the dissolved Si and Mn also start to be oxidised once [Al] and [Ti] have been depleted; (3) the extent of steel reoxidation varies with the gunning material type and less reoxidation occurs with the $\text{Al}_2\text{O}_3$ GM.

To understand the steel/gunning material interaction better, thermodynamic calculations were carried out with the aid of FactSage software. According to the above observations and measurements (Figs. 5 and 6), the FeO and $\text{SiO}_2$ impurities in the gunning material are considered to be the main sources of oxygen for steel reoxidation:

$$[\text{Al,Ti}]+\text{SiO}_2 \rightarrow [\text{Si}] + ([\text{Al,Ti}])_\text{O}_x \quad (1)$$

$$[\text{Al,Ti,Si,Mn}]+\text{FeO} \rightarrow [\text{Fe}] + ([\text{Al,Ti,Si,Mn}])_\text{O}_y \quad (2)$$

where [ ] represents the dissolved element in molten steel, wt%. During the thermodynamic calculations, 220 g of molten steel are assumed to react with gunning material at 1550°C and reach equilibrium (by using the Equilibrium module of the FactSage). The databases of FactPS, FToxid and FSstel are used in the calculation. Figure 7 shows the calculated and measured results with respect to the steel compositional changes as a function of the gunning material quantity involved in the steel reoxidation.
From the starting point of the decrease in element content (Fig. 7), the calculation depicts a clear overview of oxidation sequence for each element in molten steel, i.e. firstly [Al], followed by [Ti], [Si] and [Mn]. In the early stage of the steel/refractory interactions, a decrease in [Al] always accompanies an increase in [Si], confirming the reduction of SiO₂ (Reaction (1)). Once the [Al] and [Ti] are depleted, the [Si] and [Mn] also start to be oxidised by FeO with further steel/refractory interactions through Reaction (2). By fitting the measured Al evolution with the calculated one, the evolution of other elements can be compared with the calculations. It can be seen that except for [Si], the measured steel composition is in good agreement with the calculated value, corroborating the reliability of the present calculation. The discrepancy between the measured and calculated [Si] values is probably caused by the inaccuracy of [Si] measurement. It is difficult to completely dissolve Si in HCl solution and therefore the [Si] is not accurately measured. In addition, Fig. 7 reveals the different oxidation potentials of the two gunning materials. The calculation shows that 2.5 g of MgO GM would oxidise all 670 ppm [Al] and 360 ppm [Ti] (Fig. 7(a)), while around 9 g Al₂O₃ GM are needed to consume a similar amount of [Al] and [Ti] (Fig. 7(b)). Apparently, this is directly connected with the chemistry of gunning materials as seen in Table 2, where the reducible compounds, i.e. SiO₂ and FeO are much higher in the MgO GM (around 16 wt% in total) than that in the Al₂O₃ GM (around 5.3 wt% in total). The Al₂O₃ GM therefore has a lower oxidation capacity than the MgO GM. It should be noted that as other important oxygen sources, the air and water vapour trapped in the refractory which is related with the material porosity, are not considered in the calculation.

3.2. Effects on the Steel Cleanliness

3.2.1. General Overview of Inclusions in Steel

Figure 8 shows an overview of inclusions observed in the steel samples. Three inclusion types are mainly distinguished: (1) large Al₂O₃ and/or AlTiOX based particles with spherical shape (Fig. 8(a), around 8 μm), the number of which decreases with interaction time; (2) numerous small spherical Fe–Mn–O–S inclusions (Fig. 8(b), < 2 μm), the size of which increases during the test. Part of the large Al₂O₃ and/or AlTiOX inclusions are found to be originally present in the steel, while the small Fe–Mn–O–S inclusions are generated during the test or during steel solidification (secondary inclusions); (3) large particles with irregular shape in the steel close to the steel/refractory interface (Figs. 8(c) and 8(d), 10–20 μm). These large particles have a similar composition and structure as the gunning material, indicating they are the results of refractory erosion.

More specifically, the use of the Al₂O₃ GM containing AlTiOX impurities (Test II) causes the appearance of Al₂O₃ and/or AlTiOX clusters at the steel/refractory interface and small Ti–Al–O and Fe–Ti–Si–O inclusions in the samples with longer holding time. The Fe–Mn–S–O inclusions are much less abundant compared to Tests I and III, suggesting that the conditions during Test II are less oxidising. Figure 9 shows BSE images of the extracted inclusions from the steel sample II-3 (t = 92 min). Different inclusion morphologies and complex inclusions are observed: (1) small inclusions consisting of a TiOX shell covering a spherical SiO₂ core (< 1 μm, Fig. 9(a)); (2) large angular Al₂O₃ particles with irregular AlTiOX overgrowth (around 6 μm, Fig. 9(b)); (3) large AlTiOX aggregates (around 8 μm, Fig. 9(c)) and faceted AlTiOX inclusions with attached SiO₂ particles (Fig. 8(d)). The formation of these inclusions again relates with the oxidation sequence of elements in molten steel, i.e. [Al] is firstly oxidised to form Al₂O₃ inclusion, which acts as a core for the later precipitation. When the [Al] content is low enough, [Ti] starts to be oxidised, leading to the AlTiOX precipitates on the surface of the Al₂O₃ core (Fig. 9(b)). Once [Al] and [Ti] have been depleted, [Si] starts to be oxidised, forming SiO₂ inclusions attaching on the previously precipitated AlTiOX (Fig. 9(d)).
3.2.2. Qualitative Assessment of Inclusion Evolution

In order to quantitatively understand the inclusion evolution during the tests, SEM-AIA measurements were performed on both steel samples and steel/refractory cross sections (S/R). The results of the SEM-AIA assessment, accompanied by the total oxygen content in steel (analysed with LECO) are listed in Table 3. AIA measurements were also conducted for the original steel (TiSULC grade) to provide a reference.

Figure 10 shows the relation of inclusion area fraction and total oxygen of the steel sample. Although a scatter can be found, the data points approximately follow a linear relation (dashed line), meaning the inclusions mainly consist of oxides. Figure 11 shows the evolution of the inclusion area fraction and the total oxygen in steel as a function of time with distinct gunning materials. It can be seen firstly that the inclusion area fraction (Fig. 11(a)) and the total oxygen content in steel (Fig. 11(b)) increase with the interaction time for all three tests, indicating a continuous steel reoxidation. Secondly, considerably lower values of the inclusion area fractions and total oxygen contents are observed in the samples with Al2O3 GM compared to those with MgO and MgO + M2S GM, pointing out that the Al2O3 GM provides a less reactive condition. Moreover, plenty of smaller inclusions form in the tests with MgO based GM (type I and III) as seen from Table 3, indicating a severer steel reoxidation.

Table 3. Results of SEM-AIA analysis, where A, F.A., N and S/R represent analysed area, inclusion area fraction, inclusion number density and steel/refractory interface, respectively.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Time (min)</th>
<th>A (mm²)</th>
<th>F.A. (%)</th>
<th>N (mm⁻²)</th>
<th>Ave. dia. (μm)</th>
<th>Insoluble element content in steel (ppm)</th>
<th>T.O* (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Mn</td>
<td>Si</td>
</tr>
<tr>
<td>Original</td>
<td>0</td>
<td>109</td>
<td>0.005</td>
<td>8</td>
<td>– 0.1 0 12 8</td>
<td>–</td>
<td></td>
</tr>
<tr>
<td>I-1</td>
<td>5</td>
<td>36</td>
<td>0.030</td>
<td>33</td>
<td>9.0 0.1 0 25 69 80</td>
<td></td>
<td></td>
</tr>
<tr>
<td>I-2</td>
<td>35</td>
<td>6</td>
<td>0.115</td>
<td>296</td>
<td>3.9 134 0.2 23 30 94</td>
<td></td>
<td></td>
</tr>
<tr>
<td>I-3</td>
<td>65</td>
<td>11</td>
<td>0.100</td>
<td>172</td>
<td>5.8 307 2.4 25 8.8 321</td>
<td></td>
<td></td>
</tr>
<tr>
<td>I-S/R</td>
<td>120</td>
<td>44</td>
<td>0.198</td>
<td>108</td>
<td>18.4 759 0.3 0 0.5 468</td>
<td></td>
<td></td>
</tr>
<tr>
<td>II-1</td>
<td>29</td>
<td>33</td>
<td>0.008</td>
<td>4</td>
<td>20.7 0 0 0.3 22 65</td>
<td></td>
<td></td>
</tr>
<tr>
<td>II-2</td>
<td>59</td>
<td>30</td>
<td>0.019</td>
<td>10</td>
<td>18.5 0 0 6.7 49 39</td>
<td></td>
<td></td>
</tr>
<tr>
<td>II-3</td>
<td>92</td>
<td>17</td>
<td>0.033</td>
<td>57</td>
<td>5.9 18 5.9 79 24 73</td>
<td></td>
<td></td>
</tr>
<tr>
<td>II-S/R</td>
<td>120</td>
<td>33</td>
<td>0.043</td>
<td>38</td>
<td>11.3 26 21 41 9.6 110</td>
<td></td>
<td></td>
</tr>
<tr>
<td>III-1</td>
<td>28</td>
<td>5</td>
<td>0.110</td>
<td>248</td>
<td>4.4 142 0.3 55 65 320</td>
<td></td>
<td></td>
</tr>
<tr>
<td>III-2</td>
<td>62</td>
<td>13</td>
<td>0.047</td>
<td>133</td>
<td>3.5 149 0.5 4.6 1.9 330</td>
<td></td>
<td></td>
</tr>
<tr>
<td>III-3</td>
<td>87</td>
<td>8</td>
<td>0.082</td>
<td>209</td>
<td>3.9 247 0.3 0.3 0 425</td>
<td></td>
<td></td>
</tr>
<tr>
<td>III-S/R</td>
<td>120</td>
<td>46</td>
<td>0.257</td>
<td>137</td>
<td>18.8 934 0.5 0 0.1 451</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Total oxygen (T.O) content measured with LECO

Fig. 9. Typical morphology of inclusions found in Test II with Al2O3 GM: (a) TiOx shell covering a SiO2 core (< 1 μm), (b) irregular AlTiOx overgrowth on an Al2O3 particle (~6 μm), (c) large AlTiOx aggregate (~8 μm) and (d) faceted AlTiOx with attached SiO2 particle (~3 μm).
On the other hand, fewer inclusions with relatively larger size are found in the steel in case of Al₂O₃ GM, suggesting a steel contamination through the erosion of Al₂O₃ GM. This relatively larger size of inclusion in Test II with Al₂O₃ GM could also partially result from the agglomeration of Al₂O₃ inclusions.

3.2.3. Compositional Evolution of Inclusions

Figure 12 shows the changes in the inclusion composition as a function of the interaction time. Fig. 12(c) (Test III with MgO + M₂S gunning material) clearly reveals that: (1) Most of the inclusions are identified as Fe–Mn–O–S; (2) The non Fe–Mn–O–S inclusions (Al₂O₃, TiOₓ and/or AlTiOₓ) are mainly detected in the first sample (III-1) and parts of them are believed to be initially present in the steel before the test; (3) With the interaction, the number of inclusions increased and the inclusion composition changed from (Fe,Mn)S to (Fe,Mn)O, implying a gradual change of the molten steel during the test. Similar to Test III, Ti–Al inclusions (non Fe–Mn–O–S type) are mainly found in the early sample during Test I with MgO GM (sample I-1, Fig. 12(a)). Those Ti–Al–O inclusions are originally present in the steel. In case of Test II involving the Al₂O₃ GM (Fig. 12(b)), the steel change traced by the inclusions is, however, much milder compared to Tests I and III. The samples taken at the end of Test II contain mainly MnS and/or MnO·SiO₂ inclusions instead of (Fe,Mn)O inclusions. The differences shown in Fig. 12 suggest an outspoken influence of the gunning material on the extent of the interaction with the steel, implying distinct chemical reactivities from the gunning material. Figure 13 shows changes in the Ti/Al ratio of the inclusions during Tests I (MgO GM, Fig. 13(a)) and II (Al₂O₃ GM, Fig. 13(b)). A similar evolution route of Ti and Al in inclusions is obtained in the tests, i.e. the Ti/Al ratio first decreases and then increases during the treatment. In the final sample, the ratio levels off at around Ti/Al = 3. This evolution is believed to be due to the selective oxidation sequence of element during the experiments. Since the original steel contains around 400 ppm [Al] and 700 ppm [Ti], oxygen supplied from the gunning material preferably reacts with [Al] to form Al₂O₃ (as shown in Fig. 6). These new formed Al₂O₃ precipitated on the original TiAlOₓ inclusions, lowering their Ti/Al ratio. Once the Al content in steel decreases to a certain level, oxygen starts reacting with [Ti] to form TiOₓ inclusions, consequently the Ti/Al ratio in inclusions increases. This again confirms the composition evolution of molten steel as shown in Fig. 6. At the end of the test, the number of Ti and Al containing inclusions decreases due to inclusion floatation, while small Fe–Mn–O–S particles remain in the steel and/or form during the solidification (Fig. 12).
The insoluble contents in steel (i.e. Al, Ti, Mn and Si as non-metallic inclusion) were obtained through the SEM-AIA measurements. Figure 14 shows their change as a function of the interaction time and reveals a consistent reaction scheme for all three experiments, i.e. an on-going oxygen supply from the gunning material to the steel leading to: (1) oxidation of [Al] at first, followed by [Ti] to form Al–Ti–O inclusions; (2) precipitation of SiO2 (Fig. 8(d), SiO2 overgrowth on AlTiOx) and MnO when [Al] and [Ti] are depleted (e.g. in the case of Test I with MgO GM). Based on the change of the insoluble contents in steel, e.g. the increase of insoluble Mn and Si contents, the gunning materials can be sorted in order of increasing reactivity as: (a) Test III (MgO + M2S), (b) Test I (MgO) and (c) Test II (Al2O3). This classification implies that the redox activity of the gunning material decreases in the order: MgO + M2S > MgO > Al2O3, which is related to the level of reducible compounds in the gunning material (Table 2, in decreasing order: MgO + M2S > MgO > Al2O3). This distinct property of the gunning material has been confirmed by the evolution of the steel composition and total oxygen depicted in Figs. 6 and 10. It should be noticed that in the present tests the amount of gunning material compared with that of steel was large, providing extreme compositional exchange capacity with respect to the steel. In possible future experiments, we would, therefore, suggest to decrease the amount of gunning material relative to the level of steel.

4. Conclusions

The steel/gunning material interaction was investigated on laboratory scale. The steel cleanliness by using distinct gunning materials, i.e. Al2O3, MgO and MgO + M2S was characterised and compared. The compositional evolution of molten steel and inclusions was also predicted with thermodynamic equilibrium calculations. The main results are summarised as follow:

(1) The contact nature between the molten steel and the gunning material considerably affects their interaction behaviour. Good wetting at the interface results in severe infiltration. A large number of alumina grains are found to be eroded from the Al2O3 GM into the steel phase due to its porous structure.

(2) An FeOx layer with a thickness of 5–30 μm is formed at the steel/refractory interface due to the large difference of oxygen potential between steel and refractory. The compositional evolution of molten steel can be predicted with thermodynamic equilibrium calculations.

(3) In general, three types of inclusions are observed in the steel phase: (1) Al2O3 and/or AlTiOx inclusions, (2) numerous small Fe–Mn–O–S inclusions, and (3) large particles originating from the gunning material. Part of the Al2O3 and/or AlTiOx inclusions are believed to be originally present in the steel, while the Fe–Mn–O–S inclusions are most probably generated during the tests (reoxidation of the steel) or during solidification (secondary inclusions).

(4) The inclusion chemistry and population are highly dependent on steel/refractory interaction. More Fe–Mn–S–O inclusions are produced with gunning material containing higher reducible content, i.e. FeO and SiO2. The use of the Al2O3 gunning material containing AlTiOx impurities caused the appearance of Al2O3 and/or AlTiOx clusters at the refractory/steel interface.

(5) Although large Al2O3 inclusions were formed due to the erosion of Al2O3 GM, an improved steel cleanliness was obtained by using Al2O3 GM due to its less oxidation capacity compared to that of MgO and MgO + 2MgO-SiO2 gunning materials.

REFERENCES