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Slag formation during high-temperature interactions between SiO_2-containing refractories and iron melts with oxygen

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Refractory/metal interactions and associated reactions are significant during casting as they can lead to inclusion formation. High-temperature interactions between aluminosilicate refractories and molten steel were studied in the present investigation using the sessile drop method. The changes in the contact angles between molten iron with well-defined oxygen levels and substrates of silica, mullite ($3Al_2O_3 \cdot 2SiO_2$) as well as commercial refractories were measured in the dynamic mode. In all cases, the reaction led to slag formation.

The experiments were performed under isothermal conditions at 1823 and 1873 K. A known and constant oxygen partial pressure was imposed above the iron drop, through appropriate CO-CO_2-Ar mixtures. For all substrates, the contact angles started decreasing due to the lowering of the surface tension of iron, as oxygen was imposed on to the system. When a critical level of oxygen was reached, slag started forming at the drop/substrate interface and at this stage, the contact angle dropped suddenly. Subsequent behaviour of silica and mullite was observed to be different, with SiO_2 showing a non-wetting behaviour. In the case of SiO_2 substrate, there were also deep erosions along the periphery of the drops and there was slag accumulation at the sides of the metal drop, probably due to Marangoni flow and/or SiO(g) formation. SEM and EDS analysis of the substrates revealed that the formed slag was fayalite.

The thermodynamic criteria for slag formation and possible mechanisms of the reaction are discussed in the light of the experiments.

Key words: silica, mullite, fayalite, corundum, slag formation, sessile drop.

Introduction

The present work was initiated aiming at an understanding of the reactions between silica containing refractories and liquid iron containing well-defined amounts of oxygen. The work is of relevance to clean steel production, as the refractory erosion products can be sources of non-metallic inclusions in the steel. Erosion of refractories by steel with slightly higher amounts of oxygen, during the tapping of LD-furnace and erosion of the refractory runners during ingot casting, are the process steps where the present study is of relevance. As the refractories commonly in use are aluminosilicates, the present studies of the reactions between oxygen-containing molten iron and SiO_2 as well as mullite were initiated.

The reactions between the above-mentioned refractories and oxygen-containing iron are characterized by the formation of molten slag at the interface. The slag formation seriously affects the mechanisms of the refractory reactions and thereby has serious implications on the performance and the life of the refractories. Thus, the present paper aims at an understanding of the implications of slag formation for refractory life from a fundamental view point. The studies were carried out in micro scale by sessile drop technique, whereby, the reaction was followed by visual observation of the drop images dynamically.

Thermodynamic background

To understand the nature of the reactions of slag formation, it is crucial to have an understanding of the thermodynamics of the reactions occurring between the refractory oxides and iron containing oxygen as well as with pure iron. As part of the present work, a thermodynamic study was carried out where the stabilities of the various phases in the system Fe-O-Si were calculated using thermodynamic data in literature. From this input data, a phase stability diagram, presented in Figure 1, was constructed. The calculations showed that the two silicates likely to be formed in this system are orthosilicate and metasilicate. However, at steelmaking temperatures, only the orthosilicate or fayalite in liquid form will be the stable phase. On the other hand, as the system is cooled down, the metasilicate can precipitate. The constructed phase stability diagram shows that Fe_2SiO_4 would be formed if the oxygen content in the molten iron exceeded 0.1 wt%. This is likely to happen during certain steelmaking steps where the oxygen potential in the slag is high.

In the case of aluminosilicates, the reactions are a bit more complex. An examination of the phase diagram[1] of the system Al_2O_3-SiO_2 reveals the formation of a very stable compound, mullite, with the formula $3Al_2O_3 \cdot 2SiO_2$ as well as $2Al_2O_3 \cdot SiO_2$. The reaction and its Gibbs' energy of formation[2] for this compound are as follows:

$$3Al_2O_3 + 2SiO_2 = 3Al_2O_3 \cdot 2SiO_2 \qquad [1]$$

$$\Delta G_1^o = 18.779 - 26.953 \cdot T \qquad J \cdot mole^{-1}$$

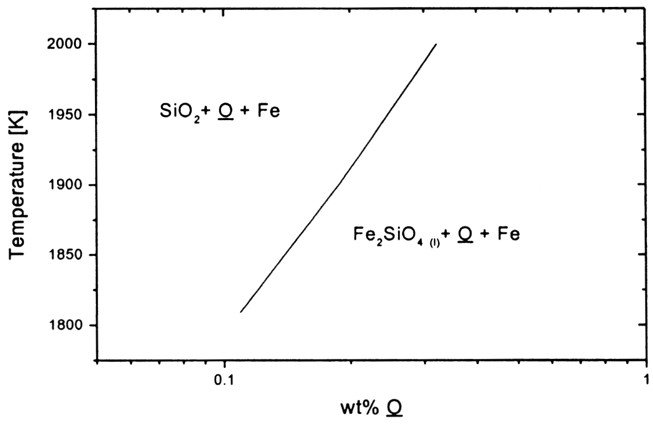

Figure 1. The phase stability diagram for the system Fe-O-si

As seen, the Gibbs energy of formation is very low and it is therefore reasonable to assume that this could be a predominant phase in the runner refractory. The reaction between molten iron containing oxygen and mullite could result in the formation of fayalite slag and hercynite ($FeAl_2O_4$) particles. The reaction and the Gibbs energy of formation[2] for fayalite are:

$$2 \cdot Fe + O_2 + SiO_2 = Fe_2SiO_4$$
$$\Delta G_2^o = -518.959 + 116.82 \cdot T \quad J \cdot mole^{-1} (\text{T range } 1000 - 1400 \ K) \qquad [2]$$

At temperatures above the melting point of iron, the silica part of mullite will react with the metal and form fayalite. As mentioned previously, the ironmetasilicate being stable at lower temperatures would not be present in the system. The Gibbs energy of formation of solid hercynite, $FeAl_2O_4$, is given by the equation[2]:

$$Fe + Al_2O_3 + \tfrac{1}{2} \cdot O_2 = FeAl_2O_4 \qquad [3]$$
$$\Delta G_3^o = -328.349 + 82.044 \cdot T \qquad J \cdot mole^{-1}$$

The phase stability diagram of the Fe-Al-O system at the steelmaking temperature has been presented earlier by the authors.[3]. When solid hercynite and liquid fayelite are formed, there is likely to be a reaction between these two and they will form a ternary slag that will have a composition that changes with temperature, according to the phase diagram FeO-Al_2O_3-SiO_2[4] presented in Figure 2. The formation and composition of this slag will not just be dependent on the thermodynamics of the reactions but also on the kinetics of the reaction.

Dynamic investigation—experimental work

In the present work, the reaction between silica containing substrate and iron drop containing oxygen were investigated on a micro level by means of the Sessile drop technique. The contact angle between the substrates and iron containing varying amounts of oxygen were investigated in static as well as in dynamic mode. The

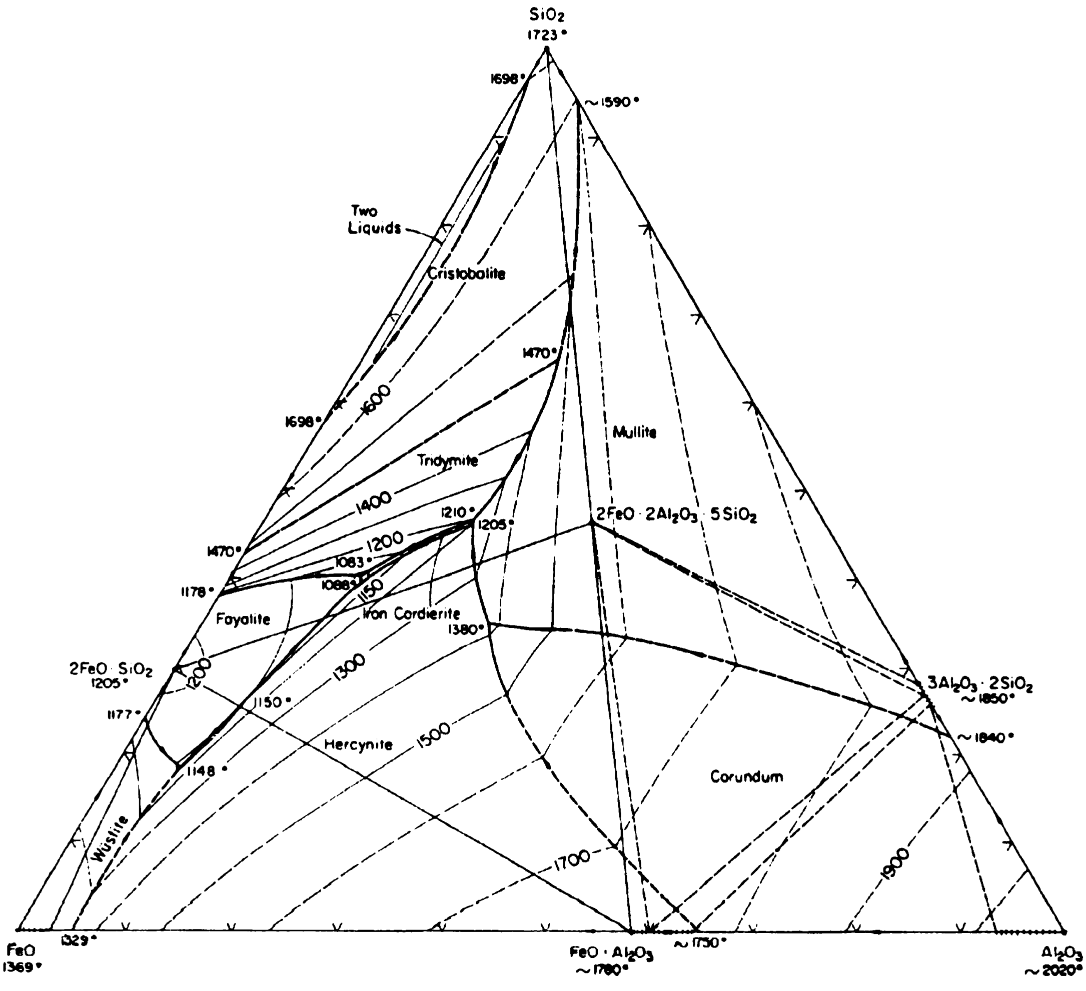

Figure 2. Phase diagram of the system FeO-Al_2O_3-SiO_2

experiments were carried out in purified argon as well as with varying oxygen partial pressures imposed on the system by means of suitable mixtures of CO, CO_2 and Ar into the system. Details regarding the furnace, the gas cleaning system as well as the image recording device have been presented elsewhere[5–6]. The change in contact angle was followed as a function of time at different temperatures.

The samples were heated up in purified argon gas and the appropriate Ar-CO-CO_2 gas mixture was then introduced into the system after the attainment of the experimental temperature. The X-ray images of the drop along with the substrate were taken in the video mode, following the changes in contact angle with time. The experimental details, the temperatures, gas ratios and their corresponding values of dissolved oxygen in molten iron, are presented in Table I. At the end of the measurements, the Ar-CO-CO_2 gas mixture was replaced by purified argon gas and the sample was then quenched. The substrate was taken out and the cross section was examined by Scanning Electron Microscope (SEM) and also through Energy Dispersive Spectroscopy (EDS). Some selected experiments were then repeated in order to confirm the reproducibility of the results.

The contact angle between the substrates and iron drop was evaluated by the video film frames obtained using a software, developed at the Department of Material Science and Engineering, Carnegie Mellon University, USA, complemented by the image analysis part developed at the Division of Metallurgy, Department of Material Science and Engineering, Royal Institute of Technology, Sweden.

Table I
Experimental sequences and their conditions

Experimental series	CO/CO_2 ratio	Targeted P_{O_2} Pa	Corresponding ppm $\underline{O}$	Temperature (K)
A	-	$< 10^{-14}$	-	1823.1873
B	0.28/0.42	$1.5 \cdot 10^{-2}$	2900	1873
B	0.28/0.42	$1.5 \cdot 10^{-2}$	1960	1823
C	0.42/0.28	$3.0 \cdot 10^{-3}$	871	1823
D	0.56/0.14	$9.9 \cdot 10^{-4}$	327	1823

Results and discussions

The experiments were carried out in purified argon gas as well as with different partial pressures of oxygen, the highest partial pressure corresponding to 0.19 wt% $\underline{O}$ at 1823 K and 0.29 wt% $\underline{O}$ as oxygen dissolved in molten iron at 1833 K, i.e. more than required to form fayelite slag according to the thermodynamic analysis.

Results with silica substrate

Images of the drops from the experimental series with the highest oxygen partial pressure and at 1833 K are presented in Figure 3. It is seen that the drop flattens as the atmosphere is changed to the gas mixture with higher oxygen partial pressure confirming, thereby, that the contact angle decreases due to the introduction of oxygen, which is surface active. An interesting observation in the present series is that the contact angle exhibits a tendency to increase after reaching a minimum point.

A reasonable explanation for the initial decrease in the contact angle would be due to the increase in the surface oxygen concentration by oxygen pick up from the gas phase. The oxygen from the surface has to diffuse into the bulk which, perhaps, would account for the plateau region. Further decrease in the contact angle is indicative of the attainment of the equilibrium oxygen concentration at the metal-substrate interface and the progress of the reaction. At this point, the drop would also have reached the equilibrium oxygen content with respect to the gas phase and enough oxygen will be present in the system for fayalite slag to form. There is a likelihood of a thin fayalite layer formation between the substrate and the drop, which would arrest the reaction. At this stage, the contact angle measured would, most probably, be between the iron drop with oxygen potential equal to that of the gas phase and the thin slag film on the silica substrate. This, evidently, is the fayalite slag formed by the following reaction:

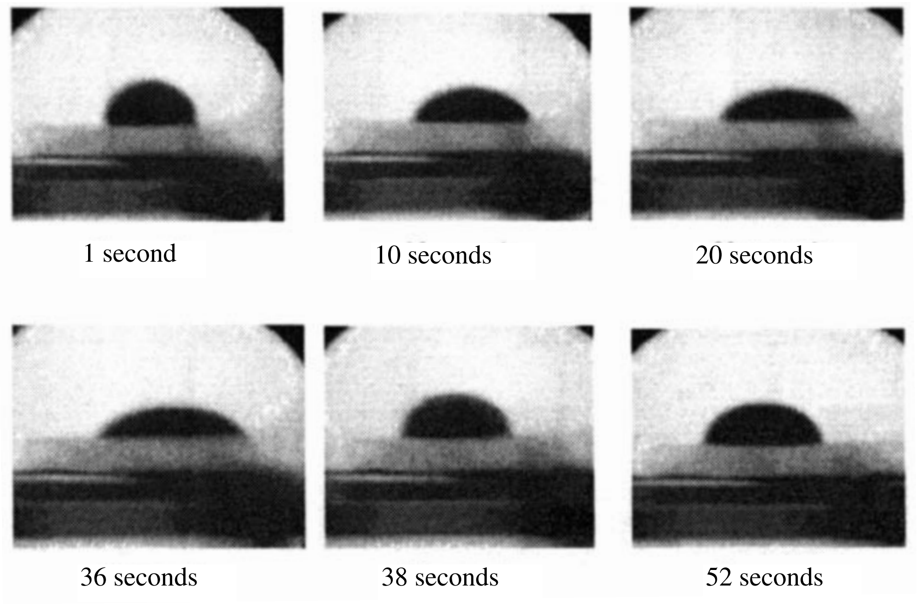
1 second
10 seconds
20 seconds
36 seconds
38 seconds
52 seconds

Figure 3. X-ray images of the sessile-drop at 1833 K at different time interval as an oxygen partial pressure of $1.5 \cdot 10^{-2}$ Pa was imposed at zero time

$$2 \cdot Fe_{(l)} + 2 \cdot \underline{O}_{(Fe,l)} + SiO_{2(s)} = Fe_2SiO_{4(l)} \qquad [4]$$

Beyond this point, the iron drop showed a tendency to move from its original position. This behaviour is likely to be due to the imbalance in the forces acting on the drop. A similar phenomenon was observed by the present authors in the case of the dynamic contact angle measurements between liquid iron and alumina substrate[3].

The SEM micrograph of the reacted drop with the substrate after the experiment at 1833 K is presented in Figure 4. The insert in the Figure shows the location of the field of vision vis-á-vis the iron drop. The low contact angle between the drop and the substrate is quite evident in this Figure. It is also seen that a thick product layer is formed by the side of the drop as mentioned earlier. The atomic ratio of iron to silicon in this layer, obtained by Electron Dispersion Spectroscopy (EDS) was close to 2, confirming that this phase was indeed the fayalite slag. The figure, on higher magnification, showed clearly the formation of dendrites in the slag. These were found to be pure SiO_2 by EDS analysis. The SEM micrographs of the drops at other oxygen partial pressures and temperatures were found to be quite similar, the amount of slag decreasing with decreasing oxygen partial pressure.

In some of the experiments, there was a preferential corrosion observed along the periphery of the drop. This may be caused by the formation and evaporation of SiO, either due to direct decomposition of SiO_2 substrate at the low oxygen potentials prevailing in the gas phase or the reaction between silicon dissolved in the liquid metal and SiO_2 substrate, both the reactions leading to the formation of SiO gas. These reactions would be dampened as the slag layer was formed around the bottom of the metal drop. Another plausible explanation is that the erosion is caused by Marangoni flow in the melt induced by differential surface tension due to concentration gradients.

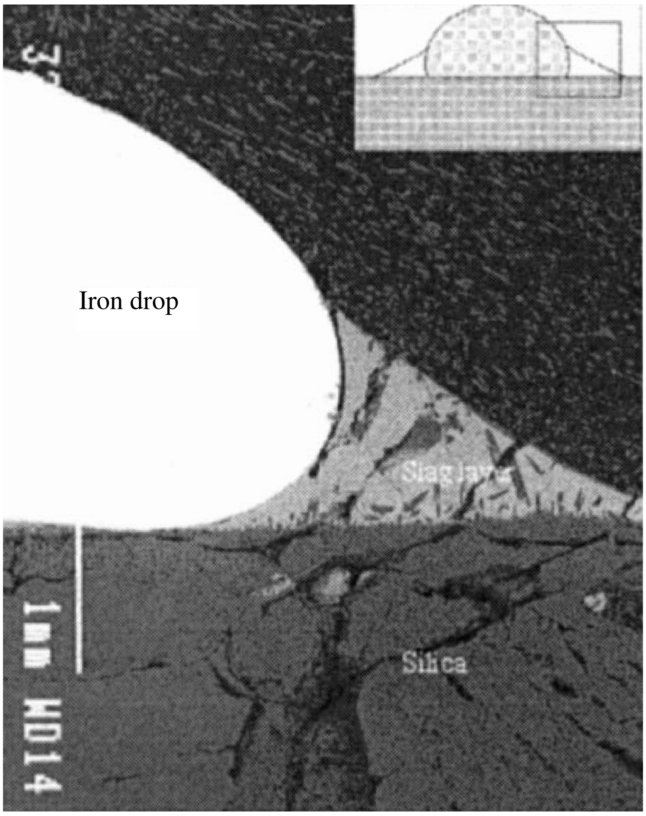

Figure 4. Photomicrograph of a section of the reacted drop and the silica substrate after the sessile-drop experiments at 1833 and oxygen partial pressure, $P_{O_2} = 1.5 \cdot 10^{-2}$ Pa

Results with Mullite Substrate

The results observed in the case of mullite, *viz.* the immediate decrease in contact angle with the introduction of the gas mixture with high oxygen potentials, the somewhat steady state when oxygen diffuses from the surface of the drop to the bulk and then the final slow drop in the contact angle were similar to those of silica substrate. However, the slag formed during the reaction between mullite and molten iron would be different from the silica system. The thermodynamic analysis shows that when mullite and iron containing some amounts of oxygen starts reacting, fayalite and hercynite will be formed. According to the ternary phase diagram presented in Figure 2, the mullite, fayalite and hercynite will start to dissolve into each other and form a slag. The composition path of the slag will go towards mullite and an intermediate phase, iron cordierite could be formed. At the experimental temperature, the ternary slag would consist of $FeO\text{-}Al_2O_3\text{-}SiO_2$, the final composition being marked as 'x' in Figure 2. If the reactions are allowed to continue, this slag will be in equilibrium with mullite and corundum. This is in agreement with the results of the SEM-EDS analyses. However, due to the kinetics of the reactions, there could still be particles of iron cordierite and hercynite as the reactions may not reach equilibrium. The composition of the slag would also change during cooling and low temperature phases could precipitate and this makes the EDS analysis of the slag very complicated and difficult.

The SEM micrograph of the reacted drop with the substrate after the experiment at 1823 K and the highest partial pressure of oxygen is presented in Figure 5. Once again, the insert in the figure shows the location of the field of vision vis-á-vis the iron drop. It is seen that the drop has reacted with the substrate and has also sunk into it. It is also seen that a molten phase has been formed and that there are free particles in this phase. The slag phase, in the figure entrapped by the molten iron, was magnified and examined

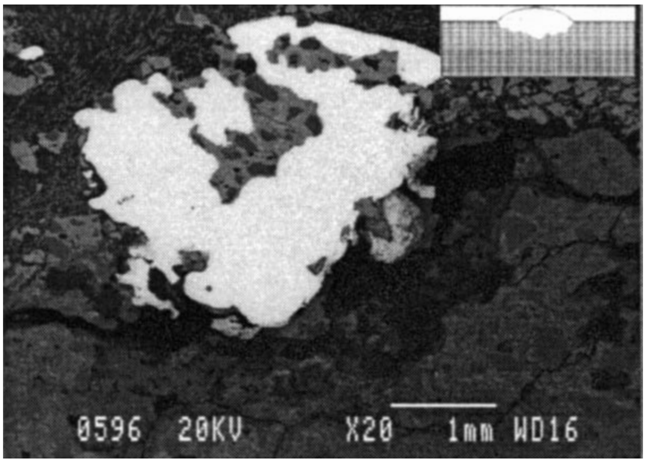

Figure 5. Photomicrograph of a section of the reacted drop and the mullite substrata after the sessile-drop experiments at 1823 and oxygen partial pressure, $P_{O_2} = 1.5 \cdot 10^{-2}$ Pa

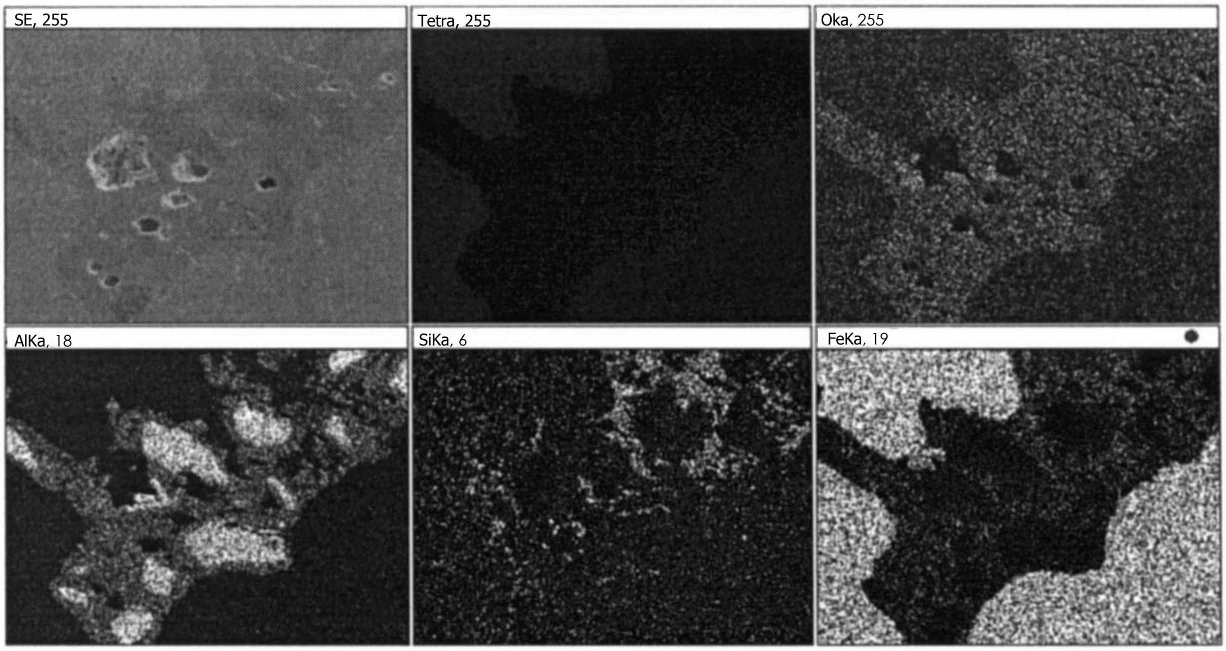

Figure 6. EDS mapping of the slag formed during reaction between mullite substrate and molten iron containing oxygen

through EDS mapping and the result is presented in Figure 6. It is seen that the slag mainly consist of alumina, silica and iron oxide. The particles are found to be alumina particles and at the periphery of these particles there is a layer containing aluminium, oxygen and iron. This layer was found to be hercynite. The EDS mapping also shows that the composition of the slag varies.

The present experimental work also showed that other factors, besides the composition of the substrate, will have an impact on the reaction mechanism. Factors like inhomogeneity, surface roughness and amounts of pores will also be of importance. The analysis of the porous mullite substrate, revealed that, along with the surface reaction with the substrate, reactions were taking place downwards into the substrate, which could escalate the slag formation and corrosion of refractories.

The present work is of great importance for the steel industry, especially for the steel plants targeting the production of clean steel. The results show that the composition of the refractory plays a great role in corrosion of the furnace linings resulting in slag formation which, in turn, can result in the formation of non-metallic inclusion in the steel matrix. The present work shows that silica, even though chemically bonded strongly in mullite, reacts with molten iron that contains some amounts of oxygen and form a slag. The formation of a thin, dense, non-wetting hercynite layer between molten iron containing oxygen and alumina substrates shows a protective influence of the presence of higher alumina contents in the lining material, leading to less reaction with steel and thereby resulting in fewer non-metallic inclusions. A distinct possibility to increase the life of the furnace linings is to coat them with a non-wetting layer, for example, hercynite. This layer would act as a barrier between the refractory and the metal and it would prevent further reactions with the refractory. Of course, the economic gain in clean steel with these changes should be compared to the higher cost of refractory production.

Summary

The present work was focused on studying the slag formation phenomenon during the reactions between oxygen-containing molten iron and aluminosilicate lining materials by means of X-ray sessile drop method. In the case of silica or mullite refractories, the reactions resulted in the formation of a slag. With silica substrate, the slag was found to be fayalite ($2FeO{\cdot}SiO_2$). In the case of mullite, the slag phase formed contained alumina. The slag formation led to non-wetting conditions and the movement of the iron drop. Preferential corrosion of the silica refractory due to possible SiO evaporation or Marangoni convection was also observed in the present study. The factors that influence the corrosion of lining materials, apart from the chemical reactions, were oxygen content in the metal, porosity and surface roughness of the refractories. The present studies are expected to lead to the development of new generation refractories, which are resistant to chemical attack by molten steel, thereby leading to lesser contamination of the steel produced by non-metallic inclusions.

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