Transient Interaction between Molten Iron, Alumina Lining Refractory and Slag

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Abstract: Laboratory experiments of the interaction between molten iron, slag and lining refractory were performed. The transient erosion and reaction with time was investigated, and thus the transient change of the reaction layer and inclusions generated in the molten iron were evaluated by using optical microscope and SEM-EDS. The transient shape and depth of the iron-slag-lining three-phase interface were measured and discussed. For alumina lining materials, the molten iron entered the lining refractory rather than the lining materials dissolved into the iron. The reaction layer included two sub-layers: Fe-rich lining layer adjacent to the iron with more FeO and less Al_2O_3, and OL-rich lining layer with more Al_2O_3 and less FeO. Without slag addition before remelting, at the top surface, a meniscus was formed between the lining refractory and the iron. FeO was generated from the reoxidation of the molten iron and FeO entered the space between the lining refractory and the iron along the meniscus. The thickness of the reaction layer increased nearly linearly with the reaction time with an erosion rate of 4.2μm/min. The existence of the FeO strengthen the erosion of the lining refractory by the molten iron.

Key words: Transient Phenomena, Molten Iron, Slag, Lining Refractory, Inclusions

1. Introduction

Non-metallic inclusions in steel have critical effect on the properties of the steel dramatically. In terms of resources, inclusions can be classified into exogenous and endogenous inclusions. Exogenous inclusions originate dominatingly from the entrapment of lining refractory and slag. For exogenous nonmetallic inclusions, the deleterious effect is more obvious due to their big size, although they are sporadic in steel [1-3]. In order to decrease exogenous inclusions in steels, it is of importance investigate the influence of ling refractory on the formation of exogenous nonmetallic inclusions.

In order to clarify the reaction among steel, slag and lining refractory, theoretical and experimental work have been carried out and reported [4-7]. Brabie investigated the mechanism of the reaction between the ling refractory and Al killed steel and found that there was a thin oxide layer at the interface due to the reaction between the magnesium vapor and the dissolved aluminum. [4] Lehmann *et al* [5] studied the interactions between the liquid steel and a MgO-based tundish refractory and reported that the reoxidation occured and the formation of an oxide layer on the refractory, mainly composed of spinel crystals and of Ca-aluminates. [5] The different lining refractories have distinct reactions with the steel. Guo *et al* indicated the steel infiltration into the refractory depended on the refractory type.[8] Severe steel infiltration occurred with the MgO material, but no infiltration was noticed with Al_2O_3 material. Good wetting at the interface resulted in severe steel infiltration, such as MgO material. They also reported that a FeO layer with a thickness of 5-30 μm was formed at the steel/lining interface.

Chang et al also reported that there was a Mg element increase in the molten steel during experiments when using MgO crucibles, indicating that Mg mass transfer occurred between the steel and the MgO-based crucible. [9]

In the current study, laboratory experiments were carried out to investigate the interaction between the molten iron, lining refractory and slag. The transient interaction with time was investigated, and thus the transient change of the reaction layer and inclusions generated in the molten iron were evaluated using the optical microscope and SEM-EDS. The transient shape and depth of the iron-slag-lining three-phase contact interface were analyzed.

2. Experimental Procedure

In the current experimental investigation， a Si-Mo electric furnace and Al_2O_3-base crucible (ID 12mm×OD 14mm×L100mm) were used for the all experiments. The temperature was set to 1873K. The details of the experiments were shown in Table 1. The electrolytic iron and slag were added in the crucibles, and then for each group 10 crucibles were put into the furnace. The crucibles were heated with the heating rate of 4.5℃/min to 1873K. After that, the temperature was kept at 1873K for two hours. The pure Ar gas was purged into the furnace during the entire experiment time. When the temperature reached 1873K, the first sample was taken out. After that, other samples were taken out every ten minutes. All samples were quenched to room temperature by air. For the group 2, only five samples were obtained because the crucibles were eroded to break by the hot slag after 50 minutes.

All the samples were mounted with crucible, and then were horizontally sectioned into two parts. The upper part was vertically sectioned. The sectioned samples were polished and observed using optical microscopy. The reaction layer between iron and lining refractory can be observed horizontally and vertically. The composition of the reaction layer and inclusions were analyzed using SEM-EDS.

Table 1. The details of the experiments

Group	Mass of electrolytic iron (g)	Mass of slag (g)	Composition of slag (mass %)
1	41	/	No slag
2	41	50	50%CaO-40% Al_2O_3-10%SiO_2

3. Results and discussions

3.1 Reaction between the lining refractory and the molten iron without the addition of slags

Figure 1 shows the vertical image of the iron-slag-lining refractory three phase contact interface at different time, and **Figure 2** is the schematic of the interface. Although no slag was added into the crucible before experiments, FeO layer was detected between the iron and the lining refractory. The FeO layer was from the reoxidation between the air and the molten iron, and then entered the space between the iron and the lining refractory. The top surface of the iron in the crucible is in a typical saddle shape, and the side is curved as a meniscus. Several layers were found from the iron to the original lining refractory layer: iron phase, FeO, transition layer, and original lining refractory layer. The thickness of the reaction layer and the height of reaction area are shown in **Table 2**. At 10 min, the average height of the area was 6.3mm, the average depths of the iron and slag entering the lining refractory were 346 μm and 769 μm, respectively. It was strange that the thickness and the depth at 10min were larger than those at 30 min and 60 min, which might be because the sample at 10 min was closer to the Si-Mo rod where the reaction was more serious due to the higher temperature closer to the heating rod. The reaction layer at 60 min was thicker than that at 30 min.

t=10min

t=30min

t=60min

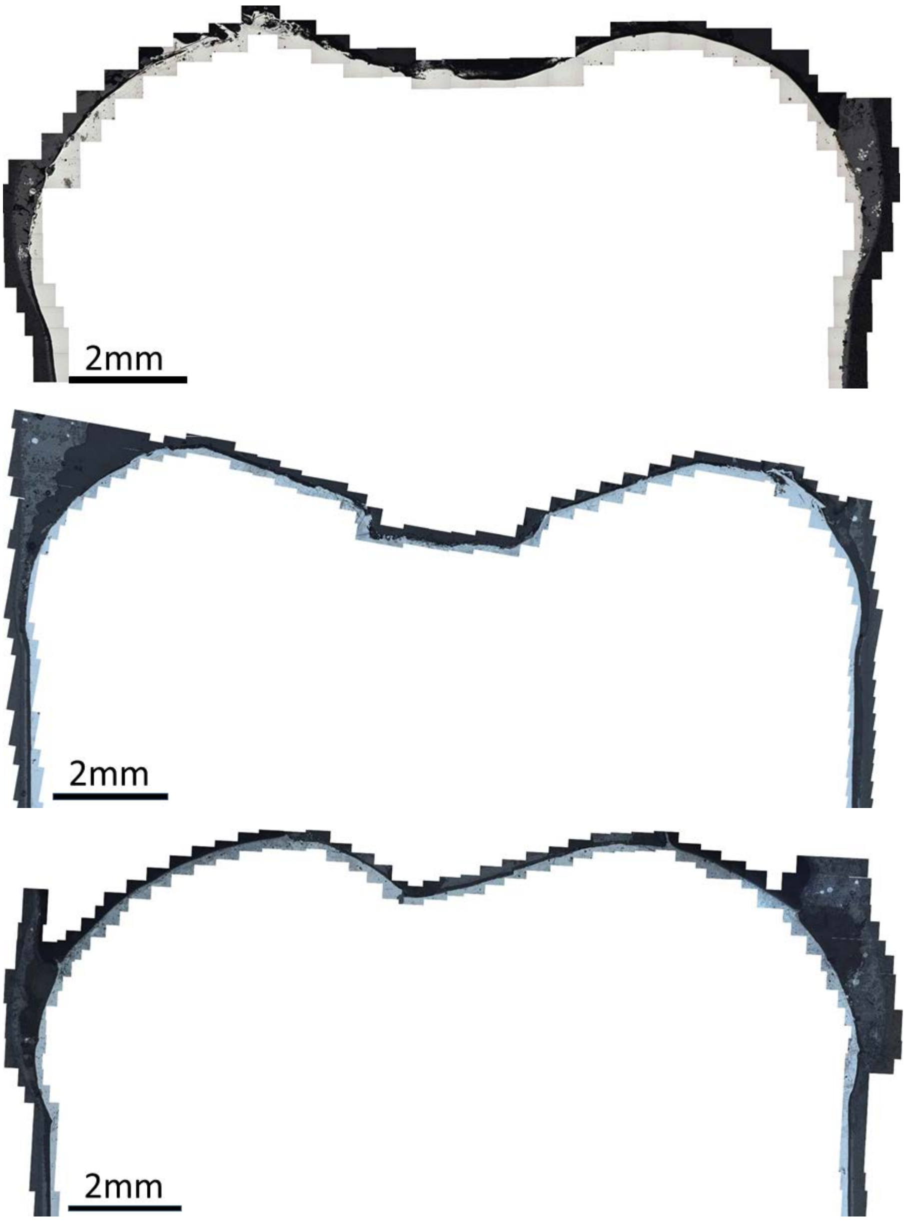


Fig.1 The interface between the iron, slag and lining refractory at different reaction time

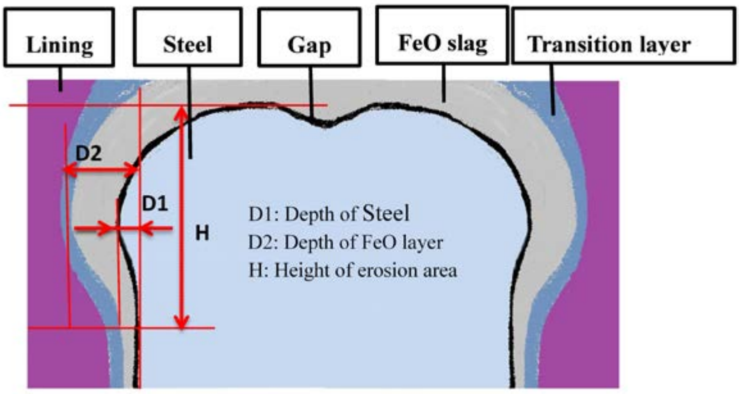
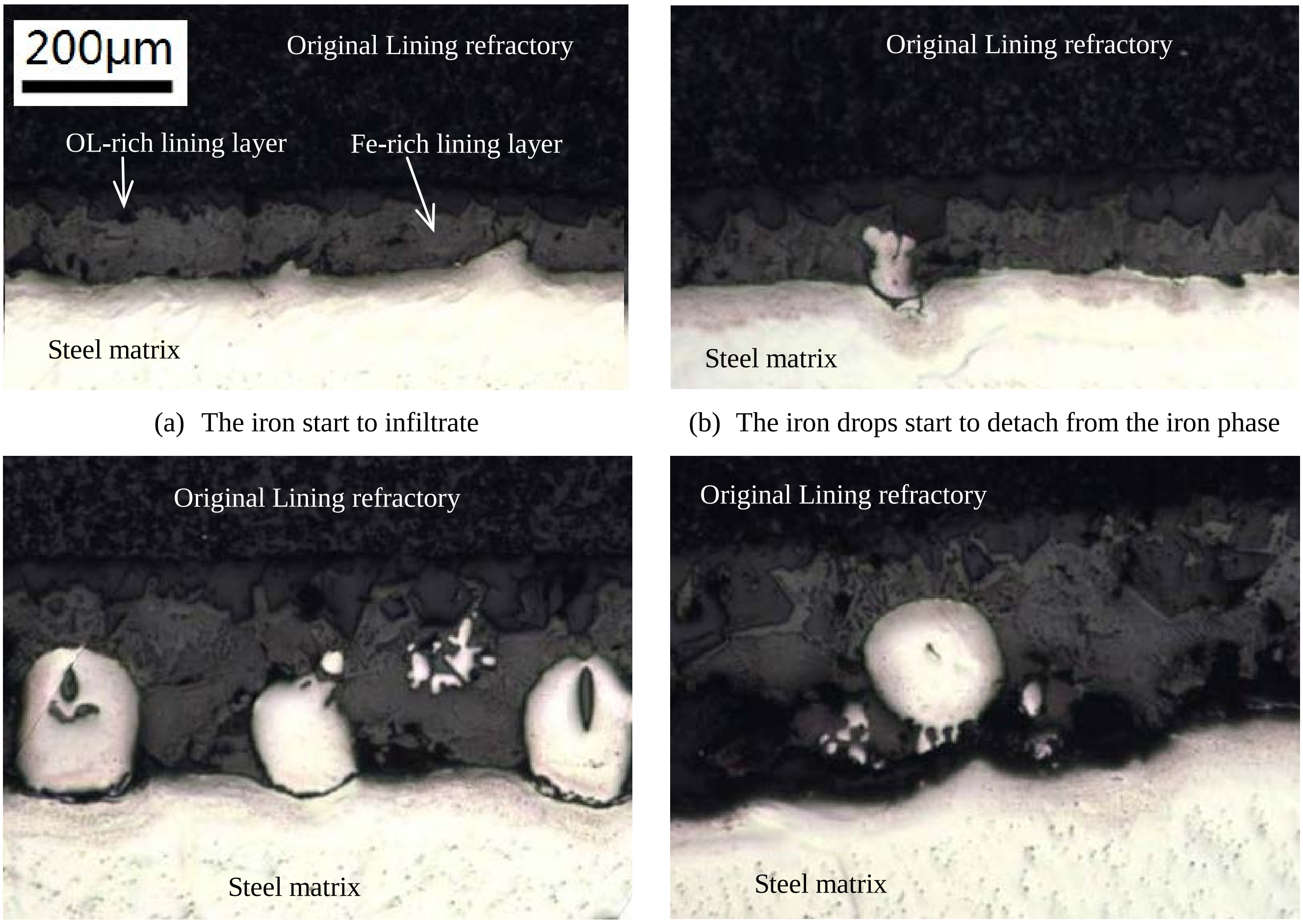


Fig.2 Schematic of the shape and depth of the iron-slag-lining three-phase contact interface

Table 2. The measured depth and height of the erosion layers

	H(μm)		D1(μm)		D2(μm)	
t=10min	6230.77	6384.62	384.62	307.69	769.23	769.23
	Mean 6307.69		Mean 346.15		Mean 769.23	
t=30min	4568.97	5086.21	86.21	129.31	344.83	431.03
	Mean 4827.59		Mean 107.76		Mean 387.93	
t=60min	6379.31	5086.21	172.41	86.21	862.07	862.07
	Mean 5732.76		Mean 129.31		Mean 862.07	

It was observed that for Al_2O_3 lining materials contacting with the molten iron, the molten iron infiltrated into the lining materials rather than the lining materials dissolved into the molten iron. **Figure 3** shows the infiltration steps. The molten iron firstly reacted with the lining refractory and generated a lining layer rich in iron adjacent to the molten iron, and then a layer rich in original lining materials (OL-rich lining layer) but also with higher Fe than the original lining materials. The interface between the Fe-rich lining layer and the original lining-rich layer was not as flat as the interface between the molten iron and the Fe-rich lining layer. Iron droplets formed at the interface between the molten iron and the Fe-rich lining layer, especially at the non-flat location such as pores, between the molten iron and the Fe-rich lining layer (**Figure 3a**); Due to the effect of surface tension and the higher potential at the molten iron side than the lining layer, the iron droplet detached into the Fe-rich lining layer, and then the molten Fe-rich lining melt entered the space interface between the molten iron and the in Fe-rich lining layer (**Figure 3b**); **Figure 3c** shows that there were several droplets formed at the interface, and the one that had entered the lining layer was broken into small pieces when they touched the interface between the Fe-rich lining layer and the original lining-rich layer since this interface is not flat, and the surface tension at the interface broke the iron droplet. **Figure 4** shows the instantaneous detach of a iron drop from the interface into the Fe-rich lining layer.



(a) The iron start to infiltrate

(b) The iron drops start to detach from the iron phase

(c) Several iron drops form at the interface and with one entering the lining phase

(d) The instantaneous detach of a iron drop into the lining phase

Fig. 3 The transient process of the molten iron infiltrating into the lining refractory of Al_2O_3-based crucible materials (80 min reaction time)

The shape and thickness of the reaction layer in horizontal direction 150mm above the bottom of the crucible is shown in **Figure 4** and the schematic is shown in **Figure 5**. As discussed above, the reaction layer contained three layers starting from the iron: the gap, the Fe-rich lining layer and an OL-rich lining layer. The interface between the iron and the Fe-rich lining layer, and the interface between the OL-rich lining layer and the original lining materials were much flatter than the interface between the Fe-rich lining layer and the OL-rich lining layer. The gap was due to the solidification shrinkage of the iron. **Table 3** and **Figure 6** show the variation of the thickness of the Fe-rich lining layer and the OL-rich lining layer. The thickness of the OL-rich lining layer increased linearly with time, but decreased sharply at 70min. While the thickness of the Fe-rich lining layer increased linearly with a small slope before 60min, but sharply increased from 69 µm to 222 µm. The total thickness of the two layers increased nearly linearly with time, with increasing rate of 4.2µm/min. **Figure 7** shows the local instantaneous image of the reaction layer at different time, clearly showing that the reaction layer became thicker and thicker with time increasing. It also shows that at some location, many iron droplets accumulated together into a line of iron, and the interface between the Fe-rich lining layer and the OL-rich lining layer was always non-flat. In the iron phase, with time increasing, more and more spherical inclusions appeared, and the SEM-EDS detection indicated that these inclusions were FeO-based which implies that they were from the reoxidation of the molten iron.

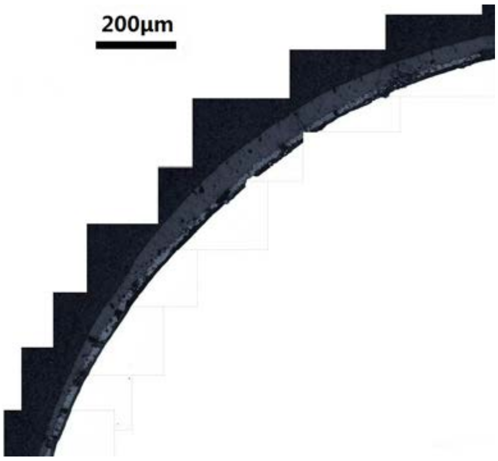


Fig. 4 Quarter of the reaction ring (t=60min)

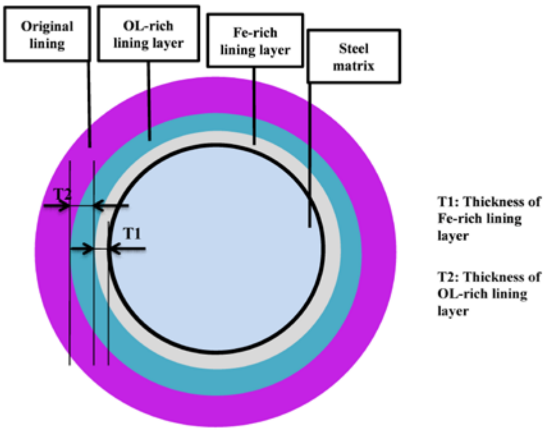


Fig. 5 Schematic of the iron-slag reaction layer

Table 3. The thickness of FeO layer and the transition layer at different time

	T1(µm)	T2(µm)	T1+T2(µm)
t=0min	13.89	55.56	69.44
t=10min	27.78	83.33	111.11
t=20min	41.67	138.89	180.56
t=30min	52.78	166.67	219.44
t=40min	55.56	277.78	291.67
t=60min	69.44	333.33	361.11
t=80min	222.22	83.33	388.89

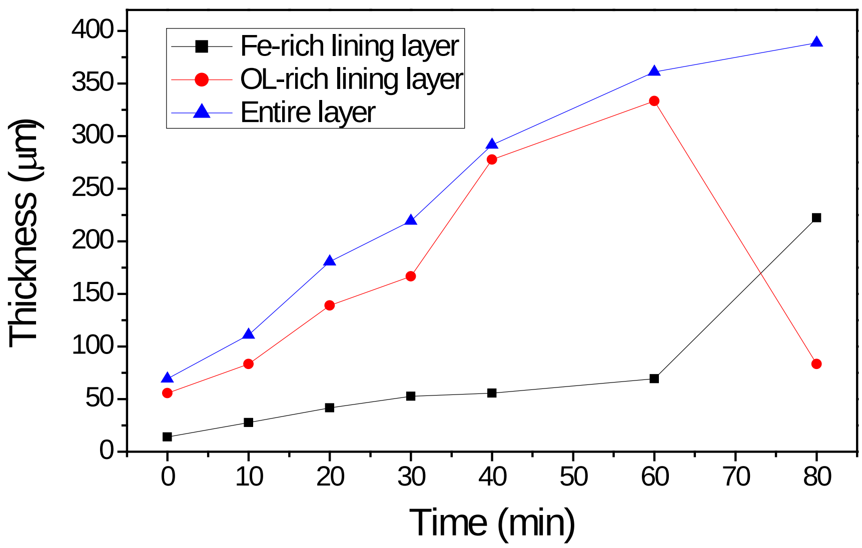
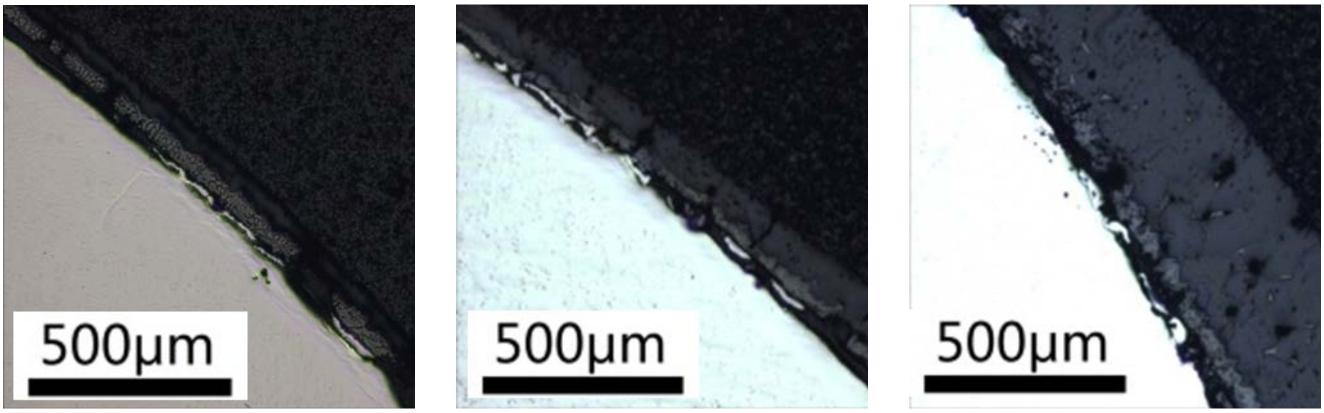


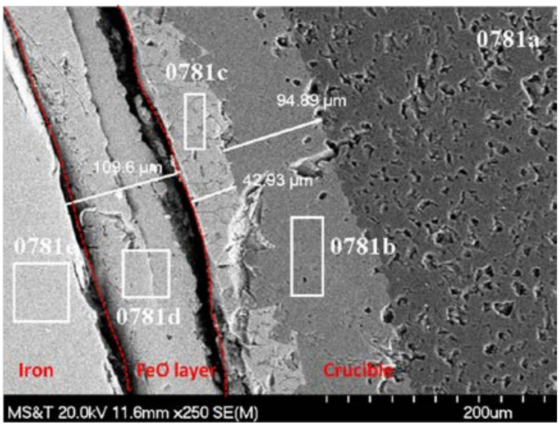
Fig. 6 Variation of the thickness of transition layer and FeO layer with time



t=10min t=30min t=60min

Fig. 7 Local morphology of the reaction layer

The phases and composition of each layer were analyzed using SEM-EDS, as shown in **Figure 8** and **Figure 9**. The composition of the four layers from the iron matrix to the original crucible materials was iron, iron oxide + little alumina, iron oxide + alumina, and pure alumina respectively. **Figure 8** clearly indicates that iron infiltrated into the lining refractory of Al_2O_3-based crucible since the concentration of Fe decreased from the iron matrix to the original lining layer. **Figure 9a** shows the morphology of the phases and their composition in the different layers: the black one was the Al_2O_3-rich phase with less FeO, and the gray one was the FeO-rich phase with less Al_2O_3. For all samples, the inclusions were mainly spherical FeO inclusions (**Figure 9b**), stemming from air reoxidation of the molten iron.



0781a: C 25.81%, O 39.72%, Al 34.04%, Fe 0.42%

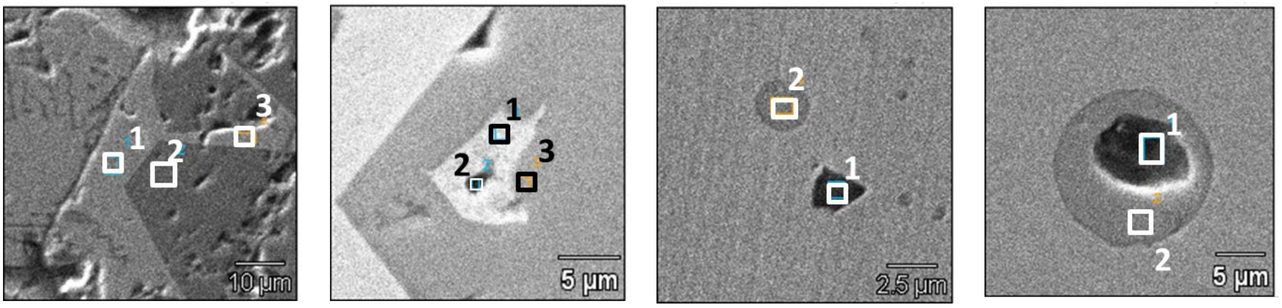
0781b: C 17.15%, O 27.33%, Al 28.53%, Fe 30.02%, Cr 0.32%, Mn 0.45%

0781c: C 22.39%, O 34.01%, Al 5.12%, Fe 35.57%, Si 1.53%, Mn 0.9%

0781d: C 39.84%, O 10.58%, Al 1.66%, Fe 47.03%, Si 0.8%, Ca 0.1%

0781e: C 25.59%, O 5.21%, Al 2.06%, Fe 67.16%

Fig. 8 Morphology and composition (atom %) of reaction layer



1. FeO: 100%
2. Al_2O_3:56%, FeO: 43%
3. FeO: 100%

1. Al_2O_3:6.7%, FeO: 93.3%
2. Al_2O_3:8.8%, FeO: 87%, SiO_2 1.3%, CaO 2.9%
3. Al_2O_3:44%, FeO:56

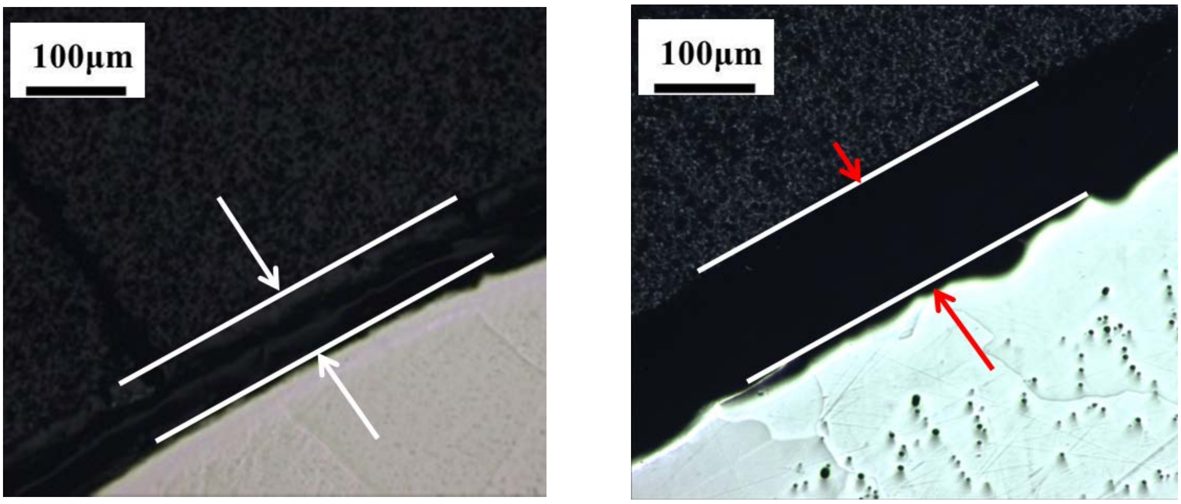
1:SiO_2, 2: FeO

1 and 2: FeO

(a) Phases and composition of the reaction layer

(b) Inclusions in iron sample

Fig. 9 Phases and composition of the reacting interface



(a) Without slag (b) With slag

Fig. 10 The comparison between two samples with and without the addition of slags

3.2 Reaction between the lining refractory and the molten iron with the addition of slags

Figures 10 shows the comparison of the reaction layer between the sample without the addition of slags and that with the addition of slag when the temperature of the iron just reached 1873K. The thickness of the reaction layer without slag addition was 70μm thick, which the one with slag addition was 97, indicating that with slag the erosion of the lining refractory was more serious than without slag. The main composition of the slag added was 50%CaO, 40% Al_2O_3, and 10%SiO_2. In additional, the size of inclusions in the sample with slag addition was larger than that without slag. More experimental investigation needs to be performed to reveal the erosion process of the lining refractory by the combined effect of the slag and the molten iron.

4. Summary

The interaction among the slag, the molten iron and the alumina lining refractory was investigated via laboratory experiments. The optical microscope and SEM-EDS were employed to observe and analyze the phases and the composition of the different layers between the iron and the original lining materials. The results indicate that for alumina lining materials, the molten iron entered the lining refractory rather than the lining materials dissolved into the iron. The reaction layer included two sub-layers: Fe-rich lining layer adjacent to the iron with more FeO and less Al_2O_3, and OL-rich lining layer with more Al_2O_3 and less FeO. The thickness of the reaction layer increased nearly linearly with the reaction time with an erosion rate of 4.2μm/min. Without slag addition before remelting, at the top surface, a meniscus was formed between the lining refractory and the iron. FeO was generated from the reoxidation of the molten iron and FeO entered the space between the lining refractory and the iron along the meniscus. The existence of the FeO strengthen the erosion of the lining refractory by the molten iron. With the addition of the slag before the remelting, the erosion of the lining refractory was more serious than without slag addition. More experiments needs to be carried out understand the erosion process of the lining refractory by the combined effect of the slag and the molten iron.

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