

INTERACTION BETWEEN MOLTEN METAL AND MgO-C REFRACTORY DURING RH DEGASSING PROCESS IN STEELMAKING

HyungBin Ji¹, YongEuy Hong¹, JaeHwan Ahn¹, Yongsug Chung^{2*}

¹Hyundai Steel Company, Dangjin-city, Rep. of Korea

*hbji@hyundai-steel.com

²Korea Polytechnic University, Siheung-city, Rep. of Korea

*ychung@kpu.ac.kr

ABSTRACT

Magnesia-carbon brick was applied to improve the lifetime of refractory for lower vessel and snorkels of RH degasser. The reaction between a molten steel and MgO-C refractory was evaluated by using cup test at 1600 °C for 3 hours in CO/CO₂ and vacuum conditions. Its result was compared with conventional MgO-Cr₂O₃ refractory. X-Ray CT analysis was carried out to observe the interface characteristics between the molten steel and the refractory. This technique provides a means for investigating the reaction area and the inner part of the sample without damaging the sample. The microstructure was analyzed by SEM to analyze corrosion reaction. In this study, a dense MgO-layer was observed at the interface between the molten steel and the MgO-C refractory. It was noted that this layer was very effective in protecting the refractory from further oxidation. Based on this observation, MgO-C refractory can be applied to RH lower vessel and snorkels.

Keywords : RH, Lower vessel, Snorkel, MgO-Cr₂O₃, MgO-C, Brick

INTRODUCTION

Increased demand for high grade steels leads to development of secondary refining technology. The RH(Ruhrstahl Heraeus) process is widely used to remove harmful gas components (H₂, O₂, N₂) which dissolved in a molten steel by vacuum treatment.

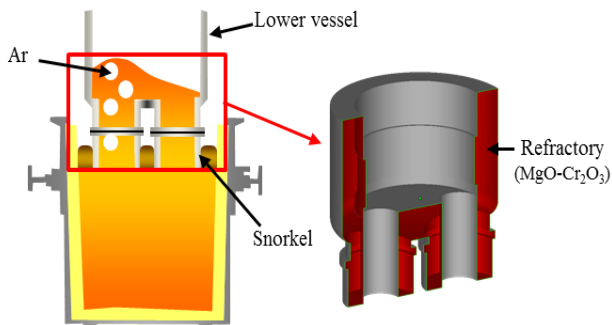


Fig. 1 RH degassing process in steelmaking

As shown in Figure 1, Magnesia-Chromite(MgO-Cr₂O₃) is currently used as a refractory material in the RH process. While MgO-Cr₂O₃ has good thermal stability and high temperature strength, corrosion by liquid oxide is severe mode of degradation which limits the lifetime.

In order to increase the life of refractory, Magnesia-Carbon(MgO-C) is one of candidates. MgO-C has excellent resistance to slag penetration and spalling at high temperature due to poor wettability of carbon and liquid oxide. While the wetted liquid slag causes erosion in MgO-Cr₂O₃ refractory, MgO-C refractory has non-wetting property with slag due to the effect of carbon in the refractory where FeO_x is not contained in the slag. Therefore, the slag does not penetrate rapidly and the refractory is prevented from erosion. However, when the FeO_x component is contained in the slag, the carbon reacts with the FeO_x in the slag, so that Fe can be reduced and the carbon can be converted into carbon monoxide or dioxide. Thereafter, as the refractory is wetted at the place where carbon was present,

the result is that erosion of the refractory is promoted.

In this study, the reaction characteristics of MgO-Cr₂O₃ and MgO-C refractories were investigated by a cup-test. Considering actual operation conditions, CO/CO₂ and vacuum atmosphere were applied. The aim of the present work is to examine the feasibility of MgO-C refractory by comparing with MgO-Cr₂O₃ refractory under industrial operating conditions.

MATERIALS AND METHODS

Refractory samples for a cup test were prepared as a crucible shape as can be seen in Figure 2. The mass ratio of molten steel and RH slag was 1 to 4. And, inner diameter of the sample was 30mm. The refractories used for the experiment were MgO-Cr₂O₃, which is currently being applied, and MgO-C, which is under investigation for substitution. Table 1 showed the chemical compositions of the refractories.

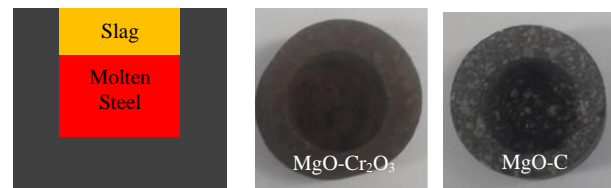


Fig. 2 Refractory samples for experiment

Table 1 Main composition of MgO-Cr₂O₃ and MgO-C refractory

Contents	Chemical composition (wt.%)			
	MgO	Cr ₂ O ₃	C	Fe ₂ O ₃
MgO-Cr ₂ O ₃	62.7	21.3	-	6.4
MgO-C	83.5	-	7.9	0.2

Considering high oxygen content in liquid iron at the initial stage of RH process, electrolytic iron specimen containing 300~400ppm oxygen was made. During performing the cup test, Ar and vacuum were applied in order to simulate industrial operating conditions. After the experiments, the depth of penetration was investigated.

The CO/CO₂ gas mixture was used to control experimental atmosphere. Using the reaction equilibrium constant (K) of CO₂(g) = CO(g)+[O], dissolved oxygen ratio (K = P_{CO}/P_{CO2}[ppmO] = 1.1×10⁴ at 1600°C) was calculated. 3wt.% CO₂, 97wt.% CO gas was used to keep the concentration of dissolved oxygen as 420 ppm in equilibrium. During RH process, vacuum is applied. Therefore, vacuum condition (1torr) was made and a typical composition of RH slag as seen in table 2 covered the metal sample.

Table 2 Main composition of slag in RH process

Composition	SiO ₂	Al ₂ O ₃	CaO	MgO	MnO	T.Fe
Wt.%	6.2	15.4	46.5	5.8	2.4	14.4

RESULTS AND DISCUSSION

1. CO/CO₂ gas(760torr) conditions

The experiment was conducted using electrolytic iron and RH slag in CO/CO₂ gas conditions. Refractories of MgO-Cr₂O₃ and MgO-C were used for the experiment. And these were kept in an electrical resistance heater for 3 hours at 1600 °C.

1.1 Specimen appearance and LECO analysis

The pictures of refractories after the experiment in CO/CO₂ gas conditions are shown in Figure 3. Because residual oxygen did not change seriously as about 400ppm, it was considered that the equilibrium experiment was well made.


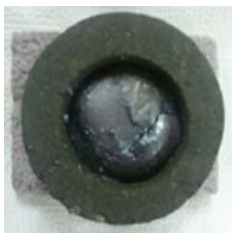


Contents	Specimen appearance	
	before	after
MgO-Cr ₂ O ₃		
MgO-C		

Fig. 3 Specimen appearance in CO/CO₂ gas conditions before and after test

1.2 Result of nondestructive inspection (X-Ray CT)

Since it was difficult to cut specimen after experiment, nondestructive inspection using X-Ray CT was conducted as shown in Figure 4. As can be seen, it was confirmed that the interface between the refractories and high oxygen electrolytic iron did not much react with each other. Since the samples contained significant oxygen, the metal samples contained pores in the sample which made while solidification.

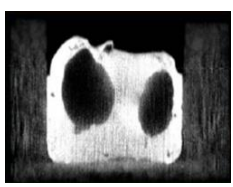
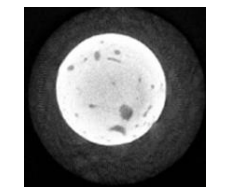
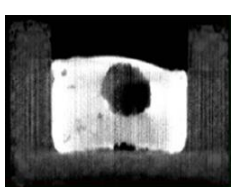
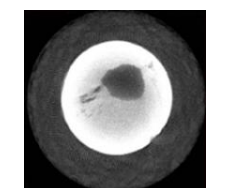
View	Side	Top
MgO-Cr ₂ O ₃		
MgO-C		

Fig. 4 Result of X-ray CT inspection (CO/CO₂ gas conditions)

2. Vacuum conditions

2.1 Specimen appearance and LECO analysis

In the case of the experiment using MgO-C refractory, it was confirmed that the residual oxygen of the electrolytic iron was greatly reduced in vacuum conditions.





Contents	Specimen appearance	
	before	after
MgO-Cr ₂ O ₃		
MgO-C		

Fig. 5 Specimen appearance in vacuum conditions before and after test

2.2 Result of nondestructive inspection (X-Ray CT)

As shown in Figure 6, the nondestructive inspection (X-Ray CT) results show that there is no significant difference between the electrolytic iron and the two refractory interfaces in the case of vacuum conditions, too.

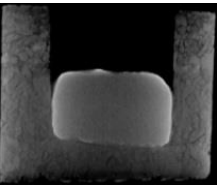
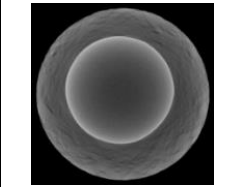
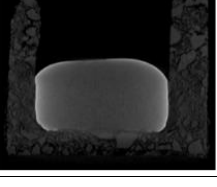
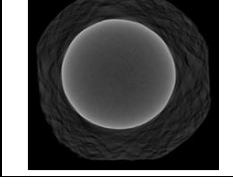
View	Side	Top
MgO-Cr ₂ O ₃		
MgO-C		

Fig. 6 Result of X-ray CT inspection (vacuum conditions)

3. FE-SEM analysis

3.1 CO/CO₂ gas conditions

Figure 7 and 8 SEM images of MgO-Cr₂O₃ and MgO-C refractories at CO/CO₂ gas conditions, respectively. In the case of MgO-Cr₂O₃ refractory, there was irregularity at the interface with electrolytic iron, and some metals penetrated into refractory. On the other hand, the MgO-C refractory had a clear interface with the electrolytic iron, and the MgO protective layer was formed between the refractory and the electrolytic iron. Table 3 and 4 showed EDX analysis in MgO-Cr₂O₃ and MgO-C refractories after the experiment, respectively. Fe was detected

in the MgO-Cr₂O₃ refractory but not founded in the MgO-C refractory. As seen in Figure 8, MgO protective layer formed at the interface between the metal and refractory. The formation of MgO formed based on the following equation and reported by former researchers[6-12].

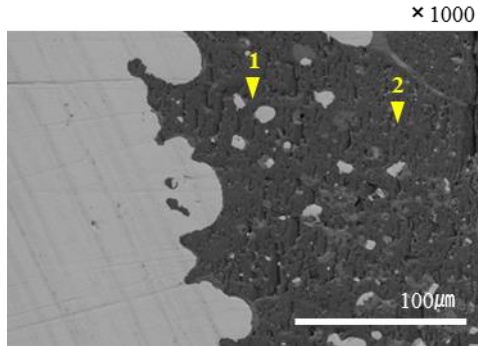


Fig. 7 SEM image of MgO-Cr₂O₃ refractory at CO/CO₂ gas conditions

Table 3 EDS analysis of MgO-Cr₂O₃ refractory at CO/CO₂ gas conditions

No.	C	O	Mg	Al	Ca	Cr	Fe
1	11.7	29.1	12.0	15.1	2.1	30.1	-
2	12.8	-	53.2	-	-	-	34.0

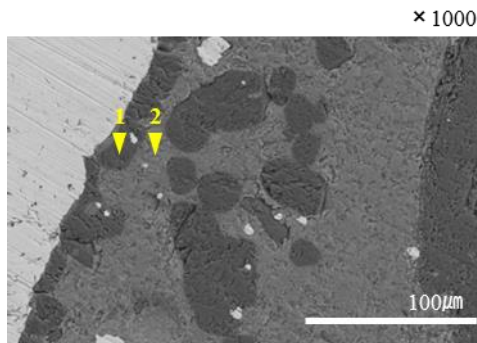


Fig. 8 SEM image of MgO-C refractory at CO/CO₂ gas conditions

Table 4 EDS analysis of MgO-C refractory at CO/CO₂ gas conditions

No.	C	O	Mg	Al	Ca	Si
1	-	30.1	69.9	-	-	-
2	7.1	31.3	-	19.3	38.4	3.9

3.2 Vacuum conditions

Figure 9 and 10 SEM images of MgO-Cr₂O₃ and MgO-C refractories at vacuum conditions, respectively. Similar trend was observed with CO/CO₂ gas conditions. Table 5 and 6 showed EDX analysis in MgO-Cr₂O₃ and MgO-C refractories after the experiment, respectively. As seen in Figure 10, MgO protective layer can be found at the interface between the metal and refractory.

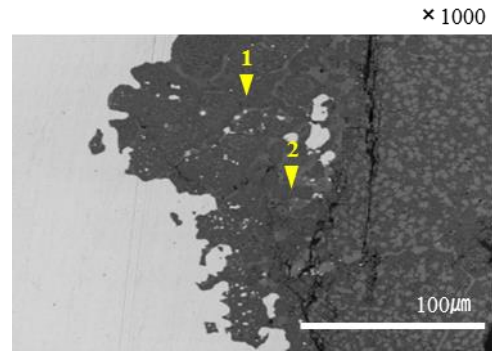


Fig. 9 SEM image of MgO-Cr₂O₃ refractory at vacuum conditions

Table 5 EDS analysis of MgO-Cr₂O₃ refractory at vacuum conditions

No.	C	O	Mg	Ca	Si
1	-	33.4	66.6	-	-
2	8.7	28.6	7.2	41.8	13.7

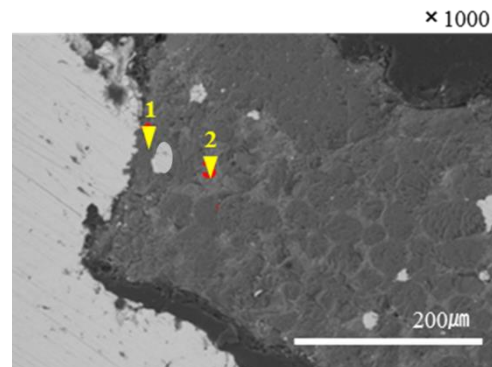


Fig. 10 SEM image of MgO-C refractory at vacuum conditions

Table 6 EDS analysis of MgO-C refractory at vacuum conditions

No.	C	O	Mg	Ca	Si
1	-	29.1	70.9	-	-
2	9.5	35.3	17.9	19.6	17.6

CONCLUSIONS

- 1) In the case of MgO-C refractory, residual oxygen content in the molten steel decreased after the experiment. This indicated that carbon in refractory and dissolved oxygen reacted. But there is no severe damage due to dense MgO protective layer.
- 2) X-ray CT results show no interface damage between MgO-Cr₂O₃/MgO-C refractories and electrolytic iron in CO/CO₂(1atm) and vacuum conditions.(1torr)
- 3) FE-SEM analysis shows that the MgO-Cr₂O₃ refractory interface is severely curved, and wear and erosion are likely to be caused by the external molten steel flow. However, MgO-C refractory seems to be stable against external flow because it has a relatively less changed interface.
- 4) On the other hand, in the case of MgO-C refractory, it is considered that the MgO protective layer is formed between the refractory and the molten steel interface by the following reaction.



- 5) In vacuum conditions (1torr), MgO protective layer was formed at the interface between MgO-C refractory and molten steel can prevent further erosion of the refractory.

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