

# Study on the corrosion mechanism between MgO-CaO refractories and refining slag

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**Abstract:** The refining AOD and VOD slag corrosion and penetration resistance of Magnesia-Calcia materials with different CaO from 22wt%-53 wt% were investigated by using static crucible technique along with visual observation, SEM and XRD measurements. The results showed that the resistance ability to corrosion and penetration of these materials decreased with the increase of CaO content in specimens. This could be due to the formation of  $C_3S$  and  $C_2S$  during the reaction between the specimen and high CaO content slag. The reaction between the molten slag and material also created a dense surface layer, which would restrain the further penetration by the slag. It was found that the depth of the layer penetrated either by AOD or VOD slag decreased with the increasing CaO content.

**Keywords:** Corrosion, mechanism, MgO-CaO refractory, refining slag

## 1. Introduction

In recent years, with the steady growth of steel production, the ladle refining process also became popular. The main processes include Argon-Oxygen Decarburisation (AOD), Vacuum Oxygen Decarburisation (VOD), LF refining Process, etc <sup>[1]</sup>. In many refining processes, from the technique and economic consideration, magnesia-calcia materials in the refining units are commonly used as the lining.

There are many reports in literature concerning the slag corrosion resistance of magnesia-calcia materials. However, most of these focused on the synthetic slag corrosion to the magnesia –calcia materials and few reports referred to the corrosion by refining slag. In the present study the present author carried out a study on the effect of CaO content in magnesia-calcia materials on the corrosion resistance to VOD and AOD slag using the static crucible method. The corrosion mechanism of the slag was also investigated. The present study would improve our understanding on the fundamentals of the relevant corrosion phenomena and provide some experimental data for developing the excellent function of high CaO materials.

## 2. Experimental

### 2.1 Sample preparation

The preparation and properties of magnesia-calcium crucibles were investigated using a pre-synthesized Magnesia-calcium clinker as raw materials. The chemical composition was listed in table 1 below. The pre-synthesized Magnesia-calcium clinker with different grain sizes were mixed homogeneously by liquid paraffin adhesives RO- II for 3~5 minutes, and then liquid paraffin was added and the mixture was milled for another 3 minutes . The mixture was shaped into a standard brick under a pressure of 150MPa at room temperature. Then it was sintered at 1650°C for 5 hrs in an electric furnace, and a hole of  $\phi 50 \times 50$ mm was drilled in the burned brick to form a crucible. The physical

properties of the crucible are as shown in Table 2. The AOD and VOD slag samples were that selected in this test, and the chemical compositions are shown in Table 3

Table.1 The chemical composition of the raw materials (wt%)

Raw material	MgO	CaO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>
Magnesia-calcium clinker1	44.35	53.60	0.73	0.89	0.43
Magnesia-calcium clinker2	74	23.50	0.62	1.10	0.78

Table.2 The physical properties of the crucible

Sample Index	CaO% (wt%)	Cold crushing strength (MPa)	Bulk density g/cm <sup>3</sup>	Apparent porosity %
MC4	53	73	3.14	7.0
MC3	49	65	3.01	7.9
MC2	42	63	3.00	8.2
MC1	22	69	2.99	8.7

Table.3 Chemical compositions of the slag samples (wt %)

Slag type	MgO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	CaO	F <sup>2-</sup>	R=C/S
VOD	13.09	10.74	31.29	37.25	3.09	1.19
AOD	6.99	5.26	26.66	59.18		2.20

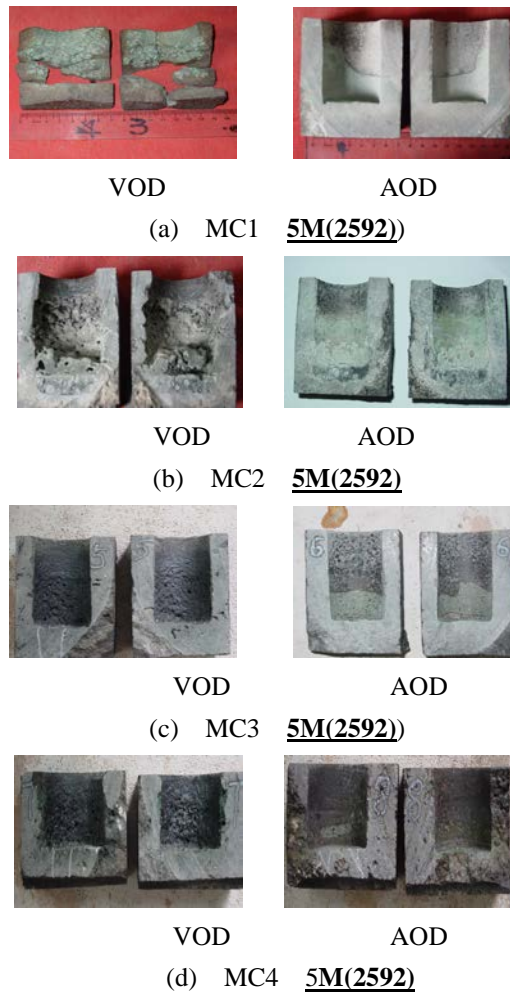
## 2.2 Slag corrosion experiment of the MgO-CaO refractories

The anti slag-corrosion experiments of the four materials were carried out respectively using static crucible techniques. For each materials, AOD and VOD slag were respectively tested. In each experimental run, the slag of 170g was filled in the crucible and tank shaped MoSi<sub>2</sub> resistance furnace adopted for heating. The crucible was heated to completely melted. Then the system was heated to 1650<sup>0</sup>C and maintained 180 minutes. After being subjected to quenching in air, the crucible was cut along the axis for photograph observation.

## 3. Results and discussion

### 3.1 Visual observation of the crucibles

After the slag corrosion test, the cross sections of the crucibles had obvious corrosion and penetration. The images were as shown in Fig 1(a) to Fig 1(d). The four cross sectional images show us that the MgO-CaO brick's corrosion and penetration resistance against AOD slag was better than against VOD slag. The VOD slag reacted with MC1 intensively and cracked the brick after the test. The AOD slag corroded MC1 slightly and there were few residual slag deposits. After reacting with the VOD slag, the MC2 to MC4 crucibles showed different degrees of corrosion and penetration.



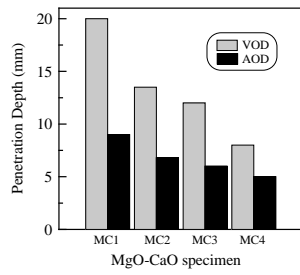
**Fig.1** The cross sectional images for each of the crucibles MC1, MC2, MC3 and MC4

### 3.2 Corrosion and penetration depth measurement

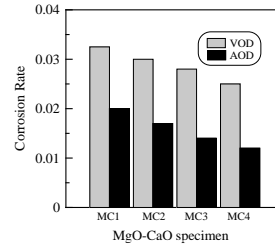
The maximum penetration depths of different crucibles with different CaO-contents were measured and the average corrosion rates were calculated and plotted respectively in Fig.2. and Fig.3

### 3.3 Slag corrosion analysis of the MgO-CaO materials

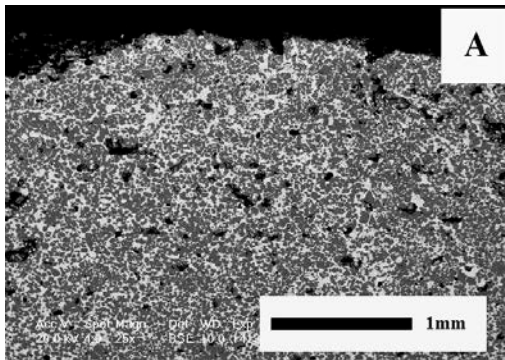
Fig.4a is the micrograph of the residual MC1 interface contacting with VOD slag. It can be seen that there was no slag adhered on the interface. Fig.4b is the micrograph of 10mm area from the interface shown in Fig.4a. It can be seen that some residual CaO spherically covered  $C_3S$ , and a lot of  $C_2S$  formed by the reaction between the matrix and the slag. Moreover, the matrix became much more compact and was almost filled with aggregates over the whole block. The slag penetrated deeply, and most of CaO in the outer layer of matrix formed  $C_2S$ . The results of XRD analysis shown in Fig.5 also proved that the volume expansion of  $C_2S$  during the phase transition could be the cause of the crucible cracked.



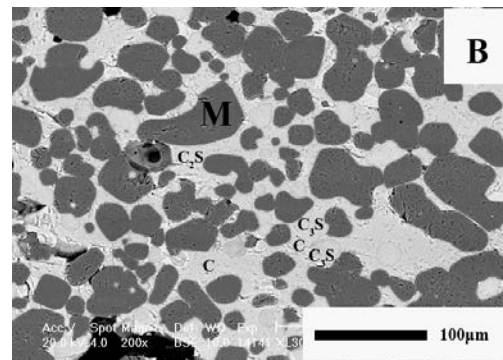
**Fig.2.** Slag penetration depths of MgO-CaO materials with different CaO contents



**Fig.3.** Average corrosion rates of materials with different CaO contents

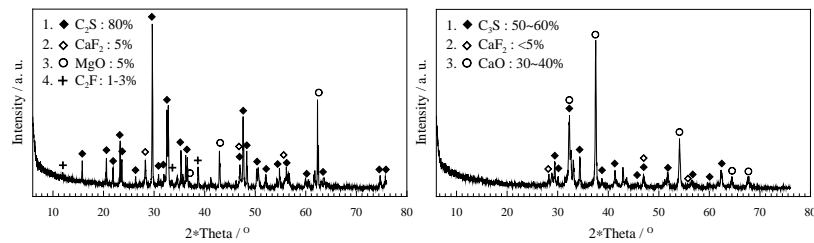


(a) Residual interface reacted with VOD slag

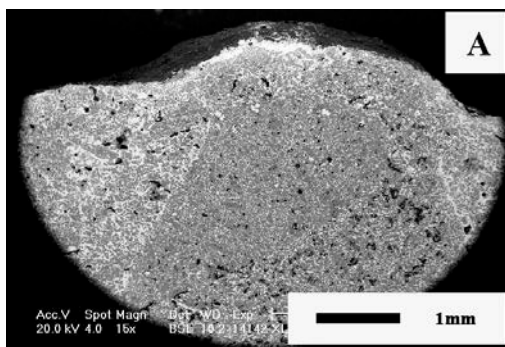


(b) 10 mm area contacting with the interface

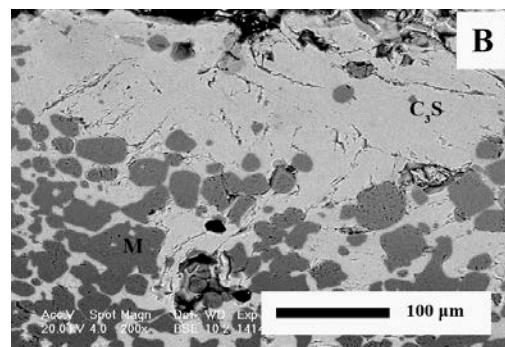
**Fig.4** The SEM micrographs of residual MC1 corroded by VOD slag



**Fig.5** The XRD pattern of residual slag after reacted with refining slag



(a) Part of the residual slag



(b) Part of the matrix

**Fig.6** The SEM micrographs of MC1 corroded by AOD slag

Fig.6a and Fig.6b are the micrographs of the residual MC1 corroded by AOD slag. Fig.9a shows a part of the residual slag. The main phase was  $C_3S$  formed by the reaction between the AOD slag and the matrix. The reaction was restricted within the zone close to surface. Fig.6b is a micrograph of a part of the matrix where less slag penetration and small reaction degree can be found. In the matrix, 5~6 mm beyond the slag surface, there was almost no penetrative slag and the matrix became a dense sinter.

### 3.4 Slag corrosion mechanism analysis

As MC1 to MC4 belong to the same materials group, the only difference lies in the different CaO content, the corrosion mechanism could be the same or similar. In the following paragraph, the author will give discuss the slag corrosion mechanisms.

As shown in Table.3, it can be seen that in addition to  $SiO_2$  and CaO, there was a small content of fluorine ions in the VOD slag, which would lower the slag melting point. The fluoride and the acidic ingredients ( $SiO_2$  and  $Al_2O_3$ ) contained in VOD slag were higher than those in AOD slag. The results of the study on the MC1 reaction with VOD slag showed that the molten VOD slag penetrated deeply into the matrix of the crucible, and most of the CaO in the outside layer of the crucible formed  $C_3S$  and  $C_2S$  with the VOD slag. The results of XRD analysis all proved this phenomenon. It has been reported that  $CaF_2$  has a destructive effect on the Magnesia-Calcia materials, and its corrosion is strong <sup>[2]</sup>. The corrosion test with different CaO content crucibles also proved this viewpoint. On the basis of the quaternary phase diagram of CaO- $SiO_2$ - $Al_2O_3$ -MgO, the saturation concentration and slag viscosity on the layer between the Magnesia-Calcia materials and slag were calculated. Either for slag AOD or for VOD slag, the corrosion rate and depth of penetration decreased with the increase of CaO content.

Regarding the mechanism of the slag-crucible reaction, it could be suggested that during the early stages of the test, the melting slag penetrated into the sidewall of the crucibles to different depths as each crucible had a different porosity. Meanwhile, the molten slag reacted with the crucible causing the crucible corrosive damaging. For the VOD slag, MC1 reacted with it intensely. The molten slag penetrated into the matrix deeper than for AOD slag and most of the CaO formed  $C_3S$  and  $C_2S$  with the slag. The crucible cracked because of the  $C_2S$  phase transition during the cooling period. For the AOD slag, all the crucibles appeared a good corrosion resistance. The reaction zone was only restricted within a thin layer close to the surface.

## 4. Conclusions

Experiments to investigate slag resistance with AOD slag and VOD slag were made using four mixtures of Magnesia-Calcia materials with different contents of CaO. The behaviour of refining slag corrosion to magnesia-calcia materials was investigated and the results are as follows:

(1) Magnesia-calcia materials corrosion and penetration resistance against AOD slag was better than against VOD slag.

(2) The process of corrosion and penetration was that, the melted slag penetrated into part of the matrix, reacted with

the matrix and then the particles of magnesia-calcium clinker were corroded. The more acidic the components ( $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$ ) in the slag, the more corrosion and penetration that appeared in the MgO-CaO refractories.

(3) No matter what kinds of slag, the depth of penetration decreases with increase of CaO content

(4) With increase in the content of CaO in magnesia-calcia materials, the slag and refractories will generate high melting point minerals of  $\text{C}_3\text{S}$  and  $\text{C}_2\text{S}$ , and these minerals prevent slag from penetrating. Consequently, they alleviate structural spalling of magnesia-calcia materials.

### References

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