STUDY ON SLAG RESISTANCE OF REFRACTORIES IN SUBMERGED ARC FURNACES MELTING FERRONICKEL

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ABSTRACT

The corrosion and penetration behaviour of magnesia-chrome brick and alumina-chrome brick in ferronickel slag was investigated by using static slag corrosion test. Compressive strength of chrome alumina brick with and without slag penetration was tested. Orthogonal experiment was designed to find the key factor affecting lining erosion and reasonable slag composition. Results showed that alumina-chrome brick has a better slag corrosion resistance property than that of magnesia-chrome brick. Mainly it is because that the Gibbs free energy of reaction between MgO and SiO_2 is smaller than that of Al_2O_3 and SiO_2. Magnesia-chrome brick has a better slag permeation resistance, the reason of which is FeO and MgO would form substitution solid solution led to the viscosity of ferronickel slag increased and permeation ability declined. The compressive strength of alumina-chrome brick with slag permeation is still larger that of magnesia-chrome brick. Alumina-chrome brick is the suitable refractory to freeze lining in submerged arc furnace. The influence order to lining corrosion and permeation are kinds of refractories, FeO content, SiO_2/MgO and basicity. The slag composition that has the minimum corrosion ability is obtained: SiO_2/MgO is 1.7, FeO is 15% and basicity is 0.85.

KEYWORDS: *magnesia-chrome brick; alumina-chrome brick; slag erosion; slag penetration; ferronickel;*

INTRODUCTION

In recent years, with the depletion of sulfide nickel mineral resources, exploration and utilization of laterite ores for producing ferronickel would be the main direction in the near future. Most of the expansion in nickel production capacity over the next ten years will come from processing of laterite ores[1]. Submerged arc furnace, SAF for short, is the main production equipment in pyro-metallurgical processing of ferronickel from laterite ores. Ferronickel slag produced from this technological process is very corrosive owing to the high proportion of SiO_2 and Fe_nO, which is one of the main reasons resulting in the breakout of furnace linings. Selecting suitable SAF refractories in ferronickel production environment and improving slag corrosion resistant of furnace wall are very important.

Magnesia-chrome bricks have been widely utilized in the steel refining process and they are also applied to the linings of SAF smelting ferronickel. Investigations of the physical properties and slag corrosion behavior of magnesia-chrome brick have been undertaken by many researchers. The dissolution mechanism of MgO and Cr_2O_3 in CaO-SiO_2-Al_2O_3-MgO-Cr_2O_3 was studied by Morita[2]. Yuan [3] studied the local corrosion of magnesia-chrome brick driven by marangoni convection at the slag-metal interface. Corrosion extent was found to decrease with the increase of MgO, FeO and Al_2O_3 contents in the slag. Ming-Hsiung Hon [4] investigated the reaction mechanisms between magnesia-chrome brick and MgO-Al_2O_3-SiO_2-CaO-FeO slag at 1923K by dynamic rotary testing and static slag corrosion test. In the slag permeated layer of MgO-Cr_2O_3 brick, CaMgSiO4 phase was founded. Alumina-chrome refractory is used in various forms such as castables and shaped refractories in blast furnaces, electric arc furnace, fiber glass furnaces, gasifiers, carbon black reactors, various corrosion resistance refractory, in cinerators and high level nuclear waste vitrification because of their superior mechanical properties, low solubility, chemical stability, slag corrosion resistance and thermal shock resistances[6]. Takehiko[7] studied the corrosion of SiO_2-CaO-B_2O_3 slag to alumina-chrome refractory. The experimental equation of corrosion rate was derived and the value of it could be calculated by basicity and viscosity of slag. Taira[8] investigated the dissolution rate of Al_2O_3 to CaO-Al_2O_3-SiO_2 slag. Corrosion extent would decrease with the rise of slag viscosity caused by the increase in CaO/Al_2O_3. Alumina-chrome brick was applied to the freeze lining of a submerged arc furnace smelting ferronickel in 2010 [9].

Magnesia-chrome brick and alumina-chrome brick have been applied to ferronickel SAF for many years. However, an extensive literature search shows that details of the corrosion reaction of these two refractories with ferronickel slag have not been studied. Besides, the comparison of applicability of these two refractories has not been carried out, reasonable component of ferronickel slag has not been discussed for prolonging the service life either.

The present work was aimed at comparing reaction of magnesia-chrome brick and alumina-chrome brick with ferronickel slag by static slag corrosion testing. The suitability of them to freeze lining was also investigated. Furthermore, reasonable slag component minimizing erosion extent to linings was obtained by orthogonal experiment design.

EXPERIMENTAL PROCEDURE

Preparation of ferronickel slag and refractory specimens

Ferronickel slag was provided by a ferroalloys manufacturer, the composition of which was determined by XRF method and listed in Table 1. Refractory specimens were selected from commercial product and their components are shown in Table 2.

Table 1. Composition of ferronickel slag, wt-%

	CaO	Fe_2O_3	MgO	SiO_2	NiO
Ferronickel slag, %	13.8	8.8	30.2	47.1	0.09

Table 2. Properties of refractories, wt-%

	MgO	SiO_2	Cr_2O_3	Al_2O_3	Others
Magnesia-chrome brick, %	63.09	0.75	20.06	10.36	5.48
Alumina-chrome brick, %	-	5.4	10.08	84.14	0.38

Static slag corrosion testing

The schematic diagram of the experimental furnace and crucible for the static slag corrosion test is illustrated in Figure 1. Refractory bricks were carved up to specimens by diamond table saw for the test (70×70×70 mm) and the hole holding slag (φ20×30 mm) was drilled in the centre of upper surface. Specimens and slag were set in the furnace and heated to the test temperature and kept for 3 hours. The test temperature is 1673K, 1773Kand 1873K, respectively. The specimens were vertically sectioned from the centre of surface for corrosion and permeation observation.

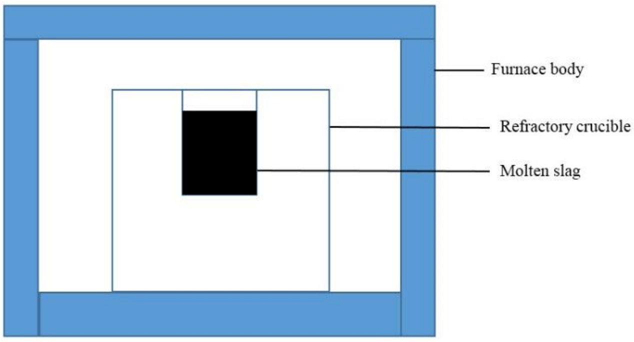


Figure 1. Schematic diagram of the corrosion test equipment

Orthogonal experiment design

The suitable composition of ferronickel slag was concluded by summarizing experience from many ferronickel manufacturing facilities. The ratio of SiO_2/MgO in slag is in the range 1.6 to 2.8. The content of FeO is about 20%~30% and the basicity of slag is within the scope of 0.85~1.15[1]. If the component of ferronickel slag is within that range, the density gap between molten slag and metal is large, the molten slag has good fluidity, therefore molten iron and slag were easily to be separated and the recovery of nickel has been improved.

The orthogonal experiment has been designed as follows. The factors of experiment are SiO_2/MgO, basicity, FeO content and kinds of refractory. Extents of corrosion and permeation to linings were defined as the index. The orthogonal experiment of four factors and two levels was designed and the data is reported in Table 3. 4-factors and 2-levels orthogonal test table could be obtained using Table 3 reported in Table 4. Eight experiments are carried out based on Table 3. The sequence of four affecting factors for lining corrosion could be known after the orthogonal experiment. At the same time, the lowest corrosion of slag composition to lining would also be obtained within the range specified in literature [1].

Table 3. The factors and levels orthogonal graph (4 factors and 2 levels)

factors / levels	FeO, wt-%	SiO_2/MgO	basicity	Kinds of refractory
1	20	1.6	0.85	Magnesia-chrome brick
2	30	2.8	1.15	Alumina-chrome brick

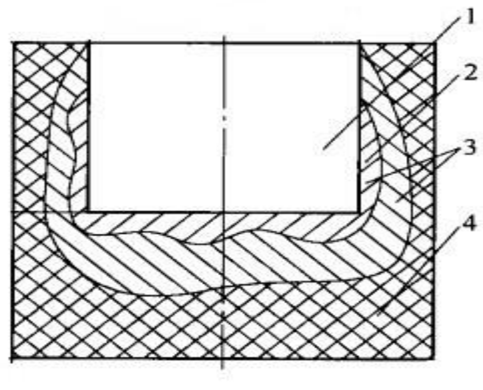
Table 4. Orthogonal test scheme table

Factors / Experiment No.	SiO_2/MgO	FeO, %	basicity	Kinds of refractory	Slag No.
1	1.6	20	0.85	Magnesia-chrome brick	1#
2	1.6	30	1.15	Magnesia-chrome brick	2#
3	2.8	20	1.15	Magnesia-chrome brick	3#
4	2.8	30	0.85	Magnesia-chrome brick	4#
5	1.6	20	0.85	Alumina-chrome brick	1#
6	1.6	30	1.15	Alumina-chrome brick	2#
7	2.8	20	1.15	Alumina-chrome brick	3#
8	2.8	30	0.85	Alumina-chrome brick	4#

RESULTS AND DISCUSSIONS

Corrosion comparison of magnesia-chrome brick and alumina-chrome brick

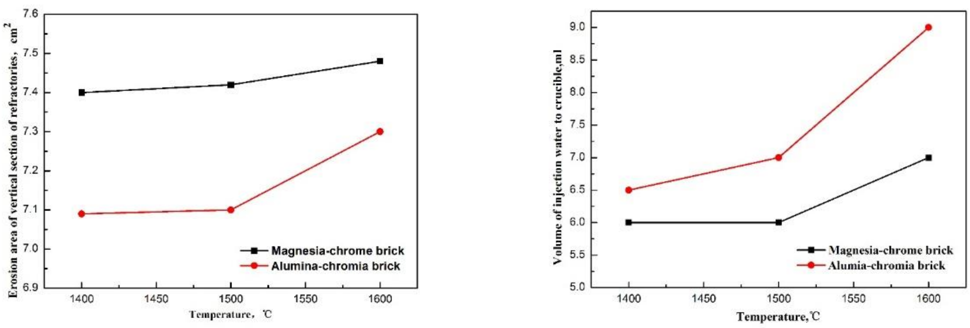
The corrosion extent of refractory bricks could be quantified by measuring the corrosion area from the vertical section, which is illustrated in Fig. 2. The permeation extent of bricks should be estimated by other method because permeating boundary is not clear sometimes. There are some residues of slag at the bottom of concave after corrosion test. The more quantities of slag residues in crucibles, the less refractory specimens have been permeated. Therefore, a certain volume of water has been injected in the slag hole of specimens. The more volume of injected water in drilling hole, the more refractory brick has been permeated.



1-crucible concave; 2-corrosion area; 3-permeation area; 4-vertical section

Figure 2. Vertical section of refractory specimen after slag corrosion test

The corrosion area and injecting water volume of these two refractories is shown in Fig.3 within a 1673K~1873K range. It could be known from Fig. 3 (a) that alumina-chrome brick has a better slag corrosion resistance property. From Fig.3 (b), magnesia-chrome brick has a better slag permeation resistance. Furthermore, the corrosion and permeation depth of these two refractories increases with the temperature increase. The corrosion and permeation extent of alumina-chrome brick was more affected by temperature than that of magnesia-chrome brick.



(a) Corrosion area (b) Permeationvolume

Figure 3. The corrosion and permeation extent of refractory specimens

The major content of magnesia-chrome brick is MgO and $MgO.Cr_2O_3$ spinel. The substitution solid solution $(Al_{2-x}Cr_x)_2O_3$ formed by alumina (Al_2O_3) and chromia (Cr_2O_3), which is the main component of alumina-chrome brick[10]. There are certain quantities of FeO in ferronickel slag. FeO and MgO would form substitution solid solution led to the FeO content decrease in slag system. The viscosity of ferronickel slag would increase because of the lower amount of FeO. Slag permeation property was inverse relationship with viscosity based Stokes-Einstein equation, which is shown as follows:

$$D = \frac{\mathrm{k}T}{6\pi\eta\,\mathrm{r}} \qquad (1),$$

Where D is the ionic diffusion coefficient, η is the viscosity of slag, T is the temperature, r is the pore diameter of refractory, k and π are constant. Therefore, magnesia-chrome brick has a better slag permeation resistance performance than alumina-chrome brick. Although MgO in magnesia-chrome brick could form the substitution solid solution with FeO to prevent slag permeation, the magnesia-chrome brick is hardly to resist the corrosion of ferronickel slag with high content of SiO_2.The Gibbs free energy of reaction between MgO and SiO_2, Al_2O_3 and SiO_2 is shown in Figure 4. It could be concluded that composite oxide at the bottom showed much more stability. It is clear that the straight line representing the reaction between MgO and SiO_2 is below the line expressing reaction between Al_2O_3 and SiO_2. Therefore, the reaction between slag and magnesia-chrome brick is relatively stronger. In addition, the Al_2O_3 in alumina-chrome brick could react with FeO to generate hercynite, the melting point of which is around 1780℃.The formation of hercynite with high melting point would enhance the resistance of alumina-chrome brick to high temperature corrosion.

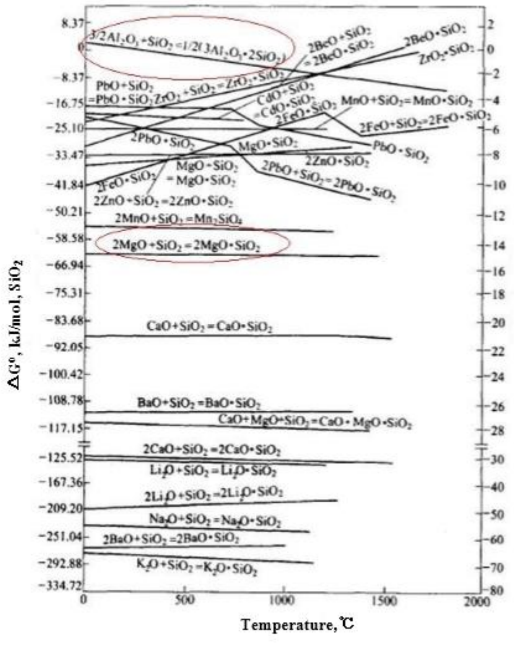


Figure 4. The relationship between Gibbs free energy for forming silicate with 1 mol SiO_2 and temperature

The alumina-chrome brick has excellent slag corrosion resistance and poor anti-permeation property. If the refractory was permeated by molten slag, the internal structure would change and the risk of producing cracks would increase. Compressive strength is an important index of refractory. Generally speaking, the compressive strength of refractory is 5~10 times higher than breaking strength. When the thermal strength is greater than breaking strength, new cracks would generate on the basis of thermal elasticity theory. It is generally known that the overall performance of linings would decline if cracks appear. In addition, other properties of refractories should also be measured. The main properties of these two refractories are shown in Tab.4.

Table 4. The main performance of magnesia-chrome brick and alumina-chrome brick

	magnesia-chrome brick	alumina-chrome brick
Density, (g/cm^3)	3.1	4.28
Porosity,%	17	20
Refractoriness under load, K	1700	1740
Cold compressive strength, Mpa	45	>150
Thermal conductivity, W/(m·K)	2.5	4.4

It could be seen that the compressive strength of alumina-chrome brick is higher than that of magnesia-chrome brick. The experiment results from Fig. 3 illustrated that slag permeation resistance of alumina-chrome brick is relatively week. Therefore, compressive strength test to the alumina-chrome bricks were carried out before and after slag corrosion experiment. Test result is shown in Fig.4. It could be found that compressive strength of alumina-chrome brick which is permeated by molten slag was still higher than that of magnesia-chrome brick. Given the data in Tab. 4, thermal conductivity of alumina-chrome brick is 1.76 times higher than that of magnesia-chrome brick. The other properties have little difference. Synthesizing each kind of properties of these two refractories, alumina-chrome brick is the suitable refractory to freeze lining in submerged arc furnace.

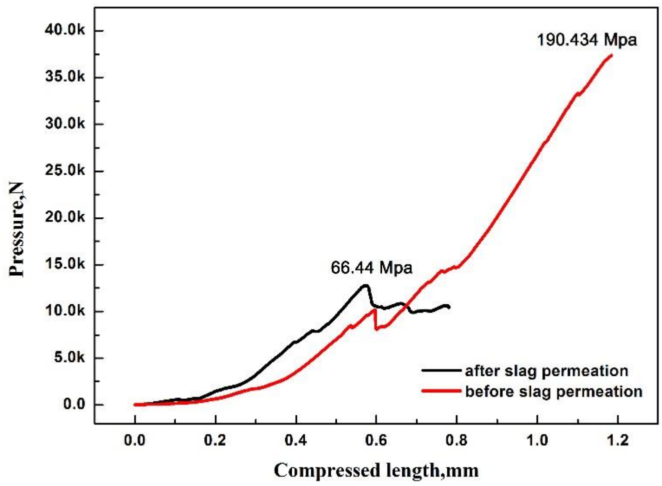


Figure 5. Thecompressive strength test for alumina-chrome brick with and without slag permeation

Orthogonal experiment with different slag composition

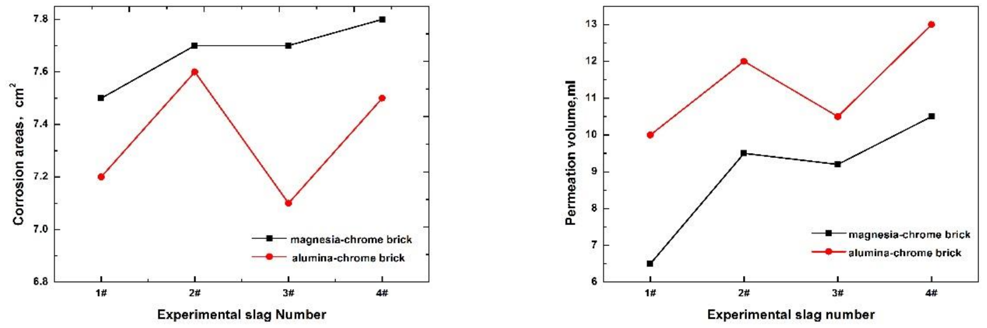
There are 8 groups of slag corrosion experiments that have been carried out with regards to the Table 3. Experiment results are shown in Fig. 5. It could be concluded that corrosion and permeation extent would be aggravated as the slag with high content of FeO. The relationship of index, corrosion areas and permeation volumes of linings, with 4 factors was studied with the extreme difference analysis. Influence trend of index by factors is shown in Fig.7. From Fig.7 (a), the line representing kinds of refractories has the maximum straight slope, which means that kinds of refractory have the biggest impact on corrosion extent. The influence order of four factors to corrosion extent is shown in equation (2).

$$Kinds\ of\ refractory > FeO\ content > basicity = \frac{SiO_2}{MgO} \quad (2)$$

Similarly, from Fig.7 (b), kinds of refractory still have the biggest impact on permeation extent, the influence rank to which is listed in equation (3).

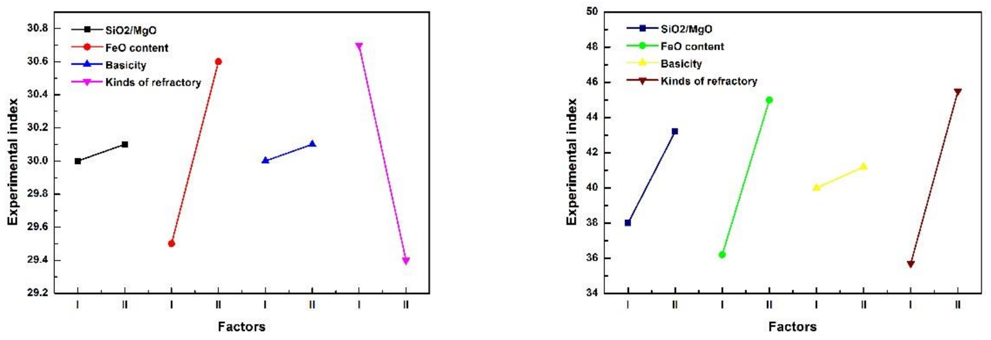
$$\text{Kinds of refractory} > \text{FeO content} > \frac{SiO_2}{MgO} > \text{basicity} \quad (3)$$

Furthermore, the slag composition, which has the lowest corrosion and permeation to linings, could also be obtained with that range from Fig. 7. The characteristics of this slag are listed as follows: SiO_2/MgO is 1.7, FeO is 15% and basicity is 0.85. The alumina-chrome brick is the suitable furnace-wall refractory for freeze lining in SAF smelting ferronickel.



(a) Corrosion area (b) Permeationvolume

Figure 6. The corrosion and permeation extent of refractories in orthogonal experiment



(a) Corrosion area (b) Permeationvolume

Figure 7. The variation trend of corrosion and permeation extent affected by factors

CONCLUSIONS

The reaction between two refractories and molten ferronickel slag using static corrosion test has been investigated. These two refractories are magnesia-chrome brick and alumina-chrome brick. The results obtained in the present study are summarized as follows:

(1) The slag permeation resistance performance of magnesia-chrome brick is higher than that of alumina-chrome brick, the main reason of which is that FeO and MgO would form substitution solid solution led to the FeO content decrease in slag system, then the viscosity of ferronickel slag would increase and permeation ability would decline.

(2) The alumina-chrome brick has better slag corrosion property at 1673K-1873K. The Gibbs free energy of reaction between MgO and SiO_2 is smaller than that of Al_2O_3 and SiO_2. In addition, the Al_2O_3 in alumina-chrome brick could react with FeO to generate hercynite, the melting point of which is around 1780℃.

(3) The measured compressive strength of alumina-chrome brick is 190.34 Mpa. This value is declined to 66.44 Mpa after molten slag permeation, which is still larger that of magnesia-chrome brick. Moreover, thermal conductivity of alumina-chrome brick is by 1.76 times bigger that of magnesia-chrome brick. Alumina-chrome brick is the suitable refractory to freeze lining in submerged arc furnace.

(4) The analysis of results of orthogonal experiment through extreme difference analysis showed that the influence order of four factors on corrosion and permeation is kinds of refractories, FeO content, SiO_2/MgO and basicity. The slag composition that has the minimum corrosion ability is shown as follows: SiO_2/MgO is 1.7, FeO is 15% and basicity is 0.85.

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