RESEARCH ON SLAG RESISTANCE OF Al_2O_3-Cr_2O_3 REFRACTORIES UNDER TEMPERATURE FLUCTUATION CONDITION

Sun Honggang[1,2,3], Li Hongxia*[1, 2,3], Li Pengtao[2, 3], Zhao Shixian[2, 3]

[1] School of materials science and engineering, University of Science and Technology Beijing, Beijing, China
[2] State Key Laboratory of Advanced Refractories, Luoyang, China
[3] Sinosteel Luoyang Institute of Refractories Research Co., Ltd., Luoyang, China
* Corresponding author's email: lihongx0622@126.com

ABSTRACT

To discuss the comprehensive effects of chromium oxide content, additives and microstructure on the slag resistance of Al_2O_3-Cr_2O_3, eight kinds of commercial Al_2O_3-Cr_2O_3 refractories were selected with Cr_2O_3 mass fraction of 10%, 12%, 30%, 50%, 60%, 75%, 90% and 95%, respectively. The corrosion resistance of Al_2O_3-Cr_2O_3 refractories was researched under the simulated thermal fluctuation condition. The results showed that the degradation of Al_2O_3-Cr_2O_3 refractories was affected by comprehensive factors, including chemical erosion, physical dissolution, thermal spalling caused by penetration. With the increase of Cr_2O_3 content, the slag corrosion rate of Al_2O_3-Cr_2O_3 material decreased, which indicated that the Cr_2O_3 content played a decisive role in the slag resistance of Al_2O_3-Cr_2O_3 material. Dense spinel layer was formed by the reaction of Cr_2O_3 with Fe_2O_3 and MgO, which had a high melting point and prevented the further infiltration of slag into the materials. Thermodynamic evaluation also showed that the content of Cr_2O_3 in refractories had a significant influence on the formation of dense spinel layer. Moreover, the additives had benefit on improving the slag penetration resistance because it effectively suppressed the microcrack propagations under the condition of temperature fluctuation. Additionally, microporous structure improved the slag penetration resistance and thermal shock resistance of the materials. Therefore, it will be also an effective way to promote slag resistance of Al_2O_3-Cr_2O_3 refractories with lower content of Cr_2O_3 by the designation and preparation of microporous structural materials.

INTRODUCTION

Al_2O_3-Cr_2O_3 refractories have been widely used in the harsh areas of thermal equipments such as petrochemical, waste-to-energy and steelmaking due to their excellent slag corrosion resistance. The extremely low solubility of chromium oxide in slag is the basic reason for the excellent slag resistance of Al_2O_3-Cr_2O_3 refractories.

Al_2O_3-Cr_2O_3 refractory is used as hot surface lining material in the service environment of high temperature (1300-1600℃), especially open parking and maintenance process bring large temperature fluctuations, so the thermal shock resistance of the material put forward higher requirements. Molten slag, which is the primary cause of Al_2O_3-Cr_2O_3 refractories degradation, has great effect on the corrosion of refractories at high temperature with thermal fluctuation. The causes of Cr_2O_3 -Al_2O_3 refractories failure and efforts to increase refractory service life for gasifier were discussed. Mechanisms involving corrosion and slag infiltration/spalling are the main causes of refractory wear[1; 2]. The reduction of slag penetration can reduce hot face lining wear[3]. Spalling and erosion are also the main causes of the damage of Al_2O_3-Cr_2O_3 refractories which have been used in smelting reduction furnace of Kwinana HIsmelt Plant in Australia[4]. Therefore, it is equally important to improve thermal shock resistance and slag resistance for Al_2O_3-Cr_2O_3 refractories. However, the normal slag resistance tests of refractory, such as static crucible method and rotary slag resistance method, have been completed under the condition of constant temperature[5]. They are ineffective to simulate thermal fluctuations in practical applications. This will greatly reduce the effectiveness of laboratory research.

Al_2O_3-Cr_2O_3 refractory is composed of matrix and aggregate. In general, the matrix is the mixture which is composed of fine powder and micro powder of aluminum oxide, chromium oxide and additives. And the aggregate is composed of different sizes particles of fused or sintered chromium oxide, corundum, chromium corundum. It is an effective way to improve the slag resistance that the content of chromium oxide of Al_2O_3-Cr_2O_3 refractories have been increased. To improve thermal shock resistance, m-ZrO_2 phase transformation toughening mechanisms present effect and microcracks produced by phase change prevent heat and mechanical stresses cracks spread in Al_2O_3-Cr_2O_3 refractories. The bricks which have micro pore structure would improve slag resistance of Al_2O_3-Cr_2O_3 refractories. In recent years, many new technologies, such as additive technology and micro porous structure design, have been greatly affected by the application of refractories. The traditional view of high performance with high chromium content will been challenged.

In this work, a variety of commercial Al_2O_3-Cr_2O_3 bricks, which had different chromium content, different additives and particular microstructure, were tested under the simulated thermal fluctuation condition using an improved rotary slag resistance test method. It would be discussed the comprehensive effects of chromium oxide content, additives and microstructure on the slag resistance of Al_2O_3-Cr_2O_3 refractories.

MATERRIALS AND METHOD

The specimens were 8 commercial refractories produced by different companies and they had different chromium content, different additives and particular microstructure. The chemical composition and physical properties of these specimens are shown in Table 1. According to the different content of chromium oxide, the specimens were numbered as 10M#, 12#, 30#, 50Z#, 60#, 75#, 85#, 90#. Among them, the specimen 10M# had a microspore structure, and the specimen 50Z# was added with zirconium mullite, the specimen 90# added with.m-ZrO_2.

Table 1 Chemical composition and physical properties of specimens

Specimens	wt%				Apparent porosity, %	Bulk density, g/cm³
	Cr_2O_3	Al_2O_3	ZrO_2	SiO_2		
10M#	10.8	82.2	--	2.0	13	3.49
12#	11.8	85.6	--	0.2	14	3.44
30#	29.8	65.6	--	--	16	3.32
50Z#	50.6	37.6	5.8	1.9	13	3.77
60#	61.3	33.2	--	--	15	3.84
75#	77.6	18.2	--	--	16	4.02
85#	87.2	5.9	--	0.2	15	4.35
90#	90.6	4.5	3.6	0.2	14	4.22

All the specimens were installed in the same rotary slag-resistant furnace (LIRR, HKZ-20), using intermittent heating process to realize the test temperature fluctuated between 200 ℃ and 1600 ℃. At first heating rotary furnace to 1 200 ℃, adding the slag, then continuing to heat up to 1600℃ and keeping 4 hours at 1600℃, stopping heating, waiting furnace to be cooled naturally to about 200 ℃. Repeating the above process 4 times, then stopping the test. The geometry and placement of the specimens are shown in Fig. 1. And the temperature change in test is shown in Fig. 2. By adding CaO-SiO_2-Al_2O_3-Fe_2O_3-MgO slag as the corrosion slag, the chemical composition of the slag is shown in Table 2.

Table 2 Composition of industrial slag for slag test

Component	MgO	Al_2O_3	SiO_2	TiO_2	CaO	Fe_2O_3
wt%	6.82	13.00	31.86	0.54	36.58	7.92

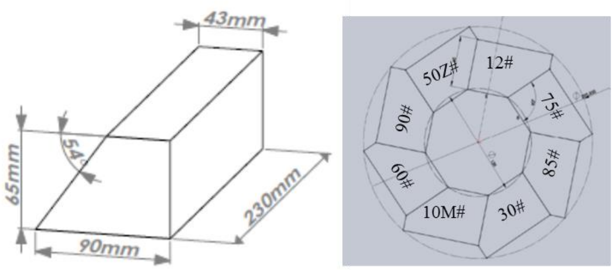

Fig. 1 Physical dimension and placement of specimens for slag test

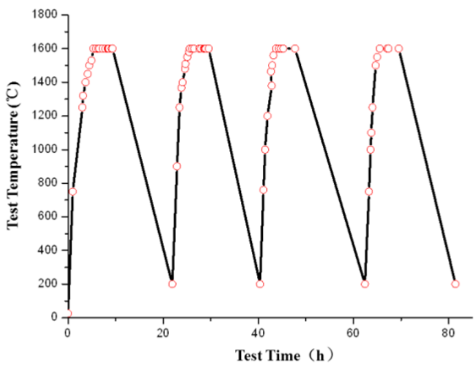

Fig. 2 Temperature change in test

After slag test, removing the specimens from the slag furnace, the fragmentation were observed, and the number of cracks were recorded. The sample sections were cut out paralleling to the 230mm×65mm plane. And the thickness of the sections was measured after the surface adhered slag was treated with hydrofluoric acid. In order to intuitively evaluate the slag erosion, index K is introduced. And K is defined as the percentage of slag thickness and initial thickness, seen as formula (1).

$$K = (L_0 - L_s)/\ L_0 \times 100 \qquad (1)$$

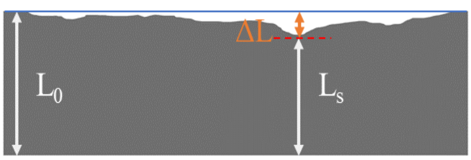

Fig. 3 Diagrammatic sketch of specimen thickness after slag resistance test

Where, L_0 represents the original width of specimens; L_s represents the minimum width of specimens after slag test. Diagrammatic sketch of specimen thickness after slag resistance test is shown in Fig. 3.

The microstructure and chemical composition of the specimens were analyzed by scanning electron microscopy (SEM, PHILIPS XL30) and energy dispersive spectroscopy (EDS, EDAX). The depth of slag penetration was deduced according to the change of microstructure and composition in SEM specimens after slag test. The pore size distribution of virgin refractories were measured by mercury porosimetry (Micromeritics AutoPore® IV 9500). The interfacial reactions of refractory materials with slag were investigated by thermodynamic modeling using FactSage™ software.

RESULTS AND DISCUSSION

1. Experimental results

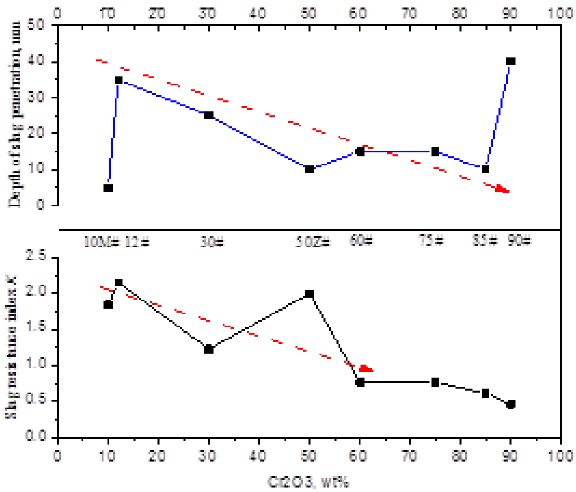

Fig. 4 Slag resistance and penetration of specimens with different chromium oxide content

Trend line

Slag resistance and penetration of specimens with different chromium oxide content is shown in Fig. 4. The erosion degree of the slag to the refractories of different chromium oxide is expressed by index K, which only reflects the relative corrosion resistance of the specimens under the same experimental conditions. As can be seen from the Fig. 4, the erosion thickness and penetration depth of the slag decrease with the increase of the content of chromium oxide in the specimens. However, the results of the specimens 10M#, 50Z# and 90# show abnormal.

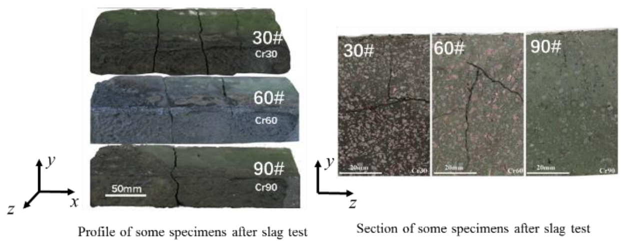

Fig. 5 Photographs of specimens after slag test

This slag experiment not only can reflect the slag resistance, but also is a good method to evaluate the thermal shock resistance of the specimens. The specimens were taken out of the furnace and cut in different directions after slag test. Photographs of individual specimens after slag test are shown in Fig. 5. The number of cracks in each section is shown in Table 3, and it is compared to the relative thermal shock resistance of specimens according to the crack number and fragmentation degree. The specimens 10M#, 50Z# and 90# show better thermal shock resistance than others, which coincide with the slag resistance.

2. Chromium oxide content

The microstructure of specimens after slag test was analyzed by SEM. And SEM analysis showed that Fe^{x+}, Mg^{2+}, Al^{3+} in the slag and Al^{3+}, Cr^{3+} in the refractory formed a spinel solid solution, which chemical structure formula is $(Mg, Fe)O{\cdot}(Al, Cr, Fe)_2O_3$, at the interface between slag and brick. The Ca^{2+}, Si^{4+}, Al^{3+} and so on in the slag formed the glass phase, which has a low melting

Table 3 Evaluation of thermal shock resistance of specimens

Crack location	Number of cracks							
Specimens	10M#	12#	30#	50Z#	60#	75#	85#	90#
Parallel to XZ	0	1	1	0	2	3	1	0
Parallel to XY	0	1	1	0	1	1	0	0
Parallel to YZ	2	4	3	2	2	2	1	1
Relative thermal shock resistance	★★★★★	★★★	★★★	★★★★★	★★	★	★★★★	★★★★★

The more stars the better thermal shock

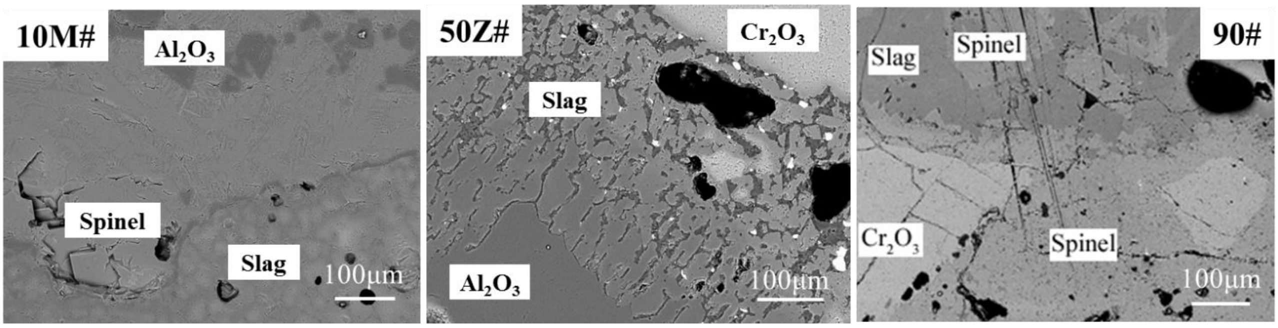

Fig. 6 SEM photos of specimens after slag test

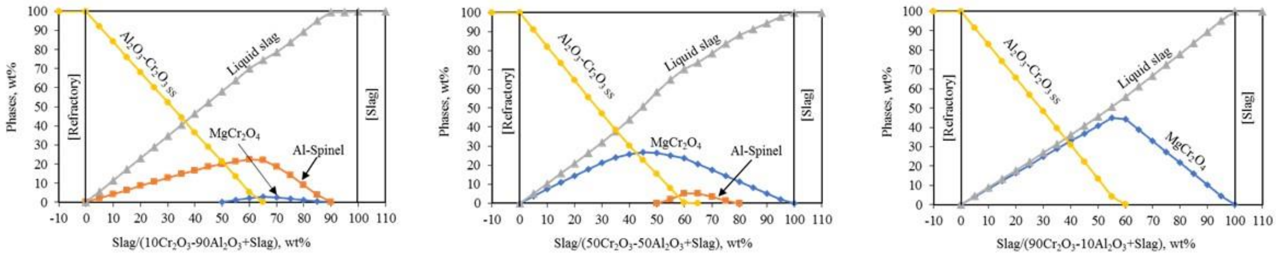

Fig. 7 Phases formed after interaction with slag on surface of (a) 10 Cr_2O_3-90 Al_2O_3, (b) 50 Cr_2O_3-50 Al_2O_3 and (c) 90 Cr_2O_3-10 Al_2O_3 refractories at 1500°C. (Note: Al-Spinel = (Mg*, Fe) Al_2O_4 where * represents a major constituent)

point, and it is easy to penetrate into the interior of the brick. The slag which have penetrated into the brick body, is easy to dissolve alumina in the brick, but the solubility of chromium oxide is very limited. As can be seen from Fig. 4, the slag resistance of Al_2O_3-Cr_2O_3 refractories is related to the content of chromium oxide. And the microstructure of three typical specimens after slag test is shown in Fig.6, which chromium oxide content are low, medium and high. In the specimen 10M#, corundum particles were dissolved and mixed with slag, and we can see the formation of new spinel phase. It is absolutely clear to effect of slag on corundum particles and chromium oxide particles in specimen 50Z#. For the 90# with high chromium oxide content, it is only found that the spinel as a new phase was formed at the interface between slag and brick. Moreover, because of the high content of SiO_2 in the specimen 50Z#, leading to the large amount of liquid phase at high temperature, the slag corrosion resistance is relatively poor.

The equilibrium phases formed after the interactions of three types of Al_2O_3-Cr_2O_3 refractory materials with molten slag at 1500°C were calculated with the FactSage^{TM} software[6]. Phases formed after interaction with slag on surface of three refractories at 1500°C is shown in Fig. 7. Calculation results indicated that $MgCr_2O_4$ as the main spinel phases was formed and remained at 1500°C in the reaction layer when the slag interacted with 50Cr_2O_3-50Al_2O_3 and 90Cr_2O_3-10Al_2O_3 refractories. However, $MgAl_2O_4$ spinel as well as slight amount of $MgCr_2O_4$ was present in the reaction products for 10Cr_2O_3-90Al_2O_3 refractory. The increasing amount of Al_2O_3 and Cr_2O_3 in the remained liquid slag after interaction implied dissolution of the refractories occurred under this condition.

3. Zirconium additive

The addition of zirconium material is one of the effective ways to improve the thermal shock resistance of Al_2O_3-Cr_2O_3 refractories[7; 8]. We can see from Table 3 that the thermal shock resistance of Al_2O_3-Cr_2O_3 refractories is independent of the content of chromium oxide. Mullite-zirconia particles were added in the 50Z#, and m-ZrO_2 micropowder as additive in the 90#. This is the reasons that they have superior thermal shock resistance.

The microstructure of specimen 50Z# is shown in Fig.8. In Fig. 8 right, the bright scaly particles are mullite-zirconia, mullite-zirconia presents a more crack morphology. Fig. 8 left shows SEM photograph of cracks in different regional of specimen 50Z# after thermal shock test. Hasselman's theory of “fracture initiation and crack extended unified theory” is that, the force of crack propagation is the elastic strain energy, crack propagation process is the gradual release of elastic strain energy and the surface energy increased payment process, once all elastic strain converted to the surface energy conversion and exhausted, cracks propagation cease.

The stage of Al_2O_3-Cr_2O_3 refractory with adding mullite-zirconia particles destroyed by thermal shock are analyzed, as shown in Fig. 9[8]. Stage 1 is the initial stage of thermal shock, due to defects in sample preparation process itself as well as local thermal stress concentration in hot-cold cycles, a plurality of microcracks are generated inside sample. In stage 2, with the increase of times of the thermal shock test, microcracks are provided enough power from constantly generated elastic strain for growth and expansion, small cracks grow large cracks, and continue to move forward inside sample. Since absorption and buffering effect of mullite-zirconia particles, cracks extension is terminated inside the particles, so the integrity of the sample is maintained. At the same time, new microcracks source is formed continuously in the sample. In stage 3, When the time of thermal shock experiments increased to a certain degree, Cracks accumulate enough power to break through the original mullite-zirconia bondage, multiple cracks intersect in the interior of the sample. Local part of sample is destroyed, while new cracks continue to repeat the process of growing up. When intersection cracks extend to the surface of the sample, the sample fragment to pieces, as seen in stage 4.

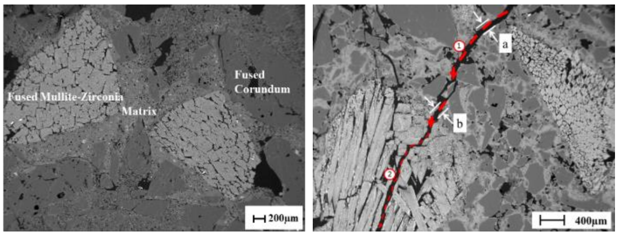

Fig. 8 The microstructure of specimen 50Z# (left: original, right: after slag test)

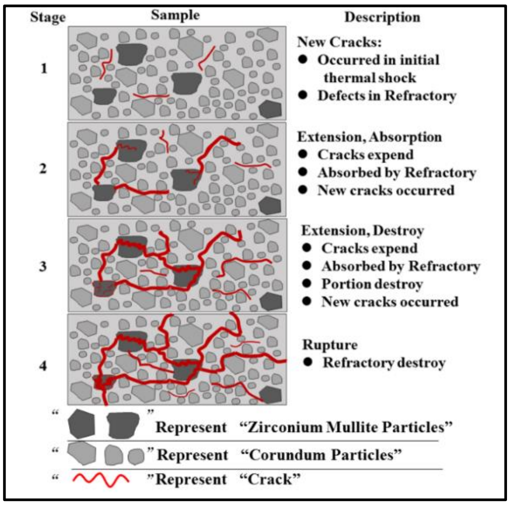

Fig. 9 The illustration of model for fused mullite-zirconia on thermal shock resistance

4. Microporous microstructure

The microstructure of refractories has a significant influence on the slag permeability. We can see from Fig.4, that specimen 10M# had the best slag penetration resistance, and specimen 90# was the worst. SEM analysis showed that chromium oxide content was too high due to poor sintering property for specimen 90#. In the matrix structure, a large number of large pores became the channel of slag infiltration.

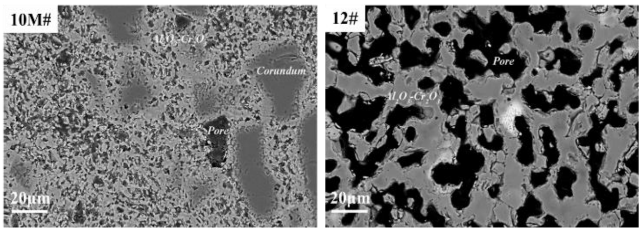

Fig. 10 Microstructure of two original Al_2O_3-Cr_2O_3 Refractories

For specimen 10Z# and 12#, which had similar chromium oxide content, the slag permeability showed a very big difference. The SEM photographs of the two specimens before slag test are shown in Fig.10. The specimen 10Z# had compact structure and microscopic pores, but the specimen 12# was the opposite. The pore size distribution of the two specimens indicated that the pore of about 2 microns in diameter accounted for more than 20% of the total pore volume in the specimen 10Z#. But in the specimen 12#, the pore size of most pores was from 5 microns to 10 microns[9]. The microporous microstructure for Al_2O_3-Cr_2O_3 refractories not only can resist the penetration of slag, but also improve the thermal shock resistance.

CONCLUSION

The character of Al_2O_3-Cr_2O_3 refractories service is affected by multiple factors such as temperature fluctuation, slag corrosion and penetration. To simulate service, some kinds of Al_2O_3-Cr_2O_3 refractories were estimated with slag resistance test under temperature fluctuation. The result showed that, slag resistance and penetration resistance increased with increasing chromium oxide content in bricks. The improvement of the thermal shock resistance was verified by introducing mullite-zirconia particles or m-ZrO_2 particles as additives into Al_2O_3-Cr_2O_3 refractories. Moreover, microporous microstructure was very favorable for both slag penetration resistance and thermal shock resistance. The addition of zirconium oxide and the microstructural design of micro pores can make up for the decline in the performance of chromium oxide in Al_2O_3-Cr_2O_3 refractories.

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