ADVANCED CORROSION TEST APPARATUS FOR REFRACTORY DEVELOPMENT

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ABSTRACT

Refractories are widely used in all high temperature processes to provide resistance to the thermal stress, physical wear and chemical corrosions. Development of advanced refractory is always a challenge to the researchers as the tests of refractories in the laboratory is difficult to truly reflect the operating conditions of the industrial furnaces. It is also risky and expensive to directly test the new materials in the industrial furnace as the replacement of the refractories will need to stop the operation, which will cause significant productivity losses. It is necessary to develop a reliable technique to perform the corrosion test of the refractory at simulated operating conditions that include temperature, oxygen partial pressure, flowing melts and reaction time. In addition, it is important to characterise the refractory and melt samples with freezed high temperature properties. An accurate simulation of the refractory corroded in the melt will provide the first hand information for the further development of refractory materials, such as the corrosion mechanism and wearing rate.

In the present study, a new dynamic corrosion test apparatus was developed to simulate the corrosions in the furnace. The atmosphere in the furnace and chamber can be controlled by inert gas or gas mixtures. Different refractory samples can be rotated in different melts with controlled speed. After certain reaction time at a given temperature, the refractory sample can be rapidly raise to the cold end of the furnace and the crucible with melt can be directly dropped into ice water. This way the reactions between the refractory and the melt are stopped and the microstructure and compositions of the phases present in the refractory and melt are freezed. The quenched refractory sample and melt can be analysed by electron probe X-ray microanalysis. The depth of the penetration, phases present and their compositions can be accurately determined.

Keywords: Rotational test, quenching, EPMA, magnesia-chromite refractory, Fe_2O_3-Al_2O_3 material

INTRODUCTION

Refractory is one of the key components in most of the high temperature processes, as it determines the life of the furnace campaign. High temperature operations require long campaign lives to decrease shut-down time so that high productivities can be achieved. The quality of refractory significantly affects the smooth production in high temperature processes. The refractories inside the furnaces are suffering hazardous environments and degrading gradually due to the thermal stress, physical wear and chemical corrosions. The thermal stress is often caused by the fluctuations in the furnace to transport heat and causing temperature imbalance. The physical wear is due to the washes of the melts with motions, and the chemical corrosions are the reactions between the refractory materials and corrosive melt at high temperatures. Development of advanced refractories having a longer service life is continuously a great challenge for the refractory material research and manufacturing.

The pyrometallurgical copper-making process is one of the major industries requiring high quality refractories. In this process a number of furnaces are involved including smelting, converting and refining. Complex gas-liquid-solid reactions occur in these furnaces at temperatures above 1100 ^oC. High-pressure gases are injected in the bath smelting furnaces, converting furnaces and refining furnaces to stir the melts for rapid reactions. In each furnace there are always several melts co-exist: slag (molten oxides), matte (molten sulphides) and/or blister (molten copper). The molten slag, matte and copper are strongly agitated inside the furnace by the injected gases. The situations are severe for the refractories as they are bearing extreme chemical corrosions by complex chemical reactions and strong physical wears. Magnesia-chrome refractory materials have been used as the linings of the furnaces in the copper industry for a long time [1-3]. Compared to other refractory materials, the magnesia-chromite type refractory shows good resistances to the slags and low thermal expansion at a wide temperature range. Recent years, new techniques and operation protocols have been developed in the modern copper making industry, such as bottom blown copper smelting furnace [4] and two-step copper making [5]. In the new technologies the refractory materials are suffering more drastic flowing conditions and complex furnace inner environments. Industrial operations show that the conventional magnesia-chromite bricks cannot meet the extreme situations with the newly developed copper making techniques implemented. New refractory materials are required to adapt the fast developing techniques on copper-making.

In the development of new refractory materials, it is essential to test new materials in the conditions similar to the industrial operations. It is practically difficult to test the new materials directly in the furnace as the replacement of the refractories will need to stop the operation, which will cause significant productivity and financial losses. It is therefore necessary to develop a technique that could simulate the furnace conditions in laboratory scale and truly reflect the corrosion to the refractory material. In addition, after high temperature reaction the refractory and melt samples need to be freezed in their microstructures and compositions. Analyses of the quenched samples will provide accurate information for the samples at high temperature. In the present study, an advanced refractory corrosion test apparatus and experimental procedures have been developed, and preliminary corrosion experiments were performed to verify the feasibility of the new technique.

ADVANCED CORROSION TEST APPRATUS

A Pyrox furnace with lanthanum chromite heating elements (maximum temperature 1650 ^oC was employed in the rotational refractory corrosion test apparatus (Fig.1). Three platforms independently controlled by three motors are located inside a sealed steel chamber. A rheometer, placed on the movable platform, rotates the refractory sample through an alumina shaft. The rheometer is connected to a computer to control the rotation speed. The crucible is suspended using an alumina tube and positioned within the hot zone of the furnace. A B-type (Pt-6%Rh/Pt-30%Rh) thermocouple is bound to the suspension tube platform, the tip of which remained adjacent to the crucible at the level where the refractory sample rotates. This enables the accurate temperature of the sample to be measured during the experiments. The rheometer and sample are sealed in a gas tight system so that the corrosion test can be carried out in accurately controlled gas atmospheres. The oxygen partial pressures inside the furnace can be precisely controlled so that different operating conditions can be simulated. There were two independent gas flow circuits (one through the chamber, and another through the furnace) to suppress heat to the chamber and protect the motors and rheometer from high temperature.

The crucible is attached to an alumina suspension tube by Pt wires. This alumina tube is fixed to the suspension platform which is independently operated to raise or lower. An alumina plunger tube having the same diameter as the crucible is attached to a fixed plunger platform. The bottom of the furnace is sealed by a steel lid with glass window which is used to monitor the position of the crucible and thermocouple during the test. After the test, the lid at the bottom of the furnace is removed and replaced by plastic film. When the quenching mechanism is activated, the suspension tube controlled by the platform is raised and then the upper edge of the crucible touched the bottom end of the plunger tube. The soft Pt wires connecting the crucible and suspension tube are sheared by the plunger tube to enable the crucible to drop directly into the water bucket beneath the furnace.

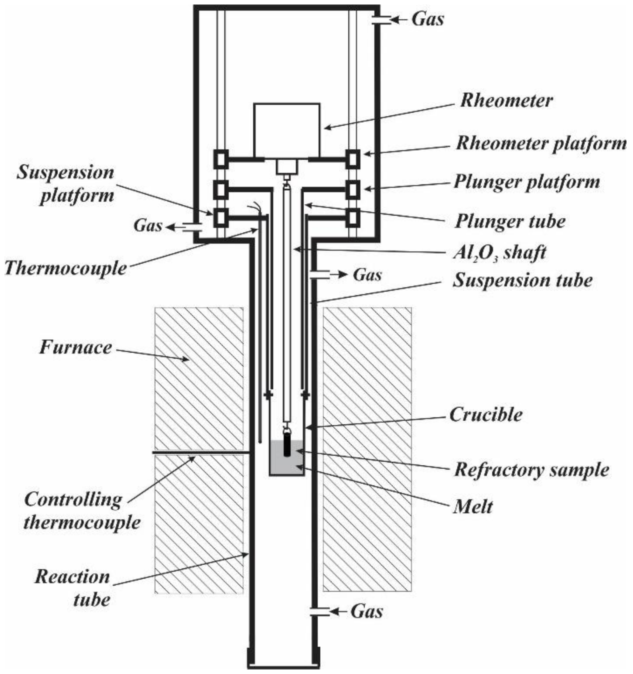

Fig. 1. Schematic of the high temperature rotational refractory corrosion test apparatus

Fig. 2 provides dimensional details of the cylindrical crucible and refractory sample used in the corrosion test. The crucible with inner diameter Φ25 mm and 87.5 mm height (43 mL in volume) is employed to hold the liquid melt. The material of the crucible can be metal (platinum, iron, molybdenum) or oxide (alumina, magnesia) depending on the melt to be used. Usually for metal or matte a oxide crucible is used. Both metal and oxide may be used for the test involving slag. The composition of the melt may change during the test. However, post-experiment analysis of the quenched sample will be able to accurately measure the final composition. Approximated 30 mL of the melt is required to provide sufficient liquid level for the test. The melt is prepared in a separate furnace and the liquid level needs to be determined accurately before the test. The refractory sample is made to a regular shape and fixed to the alumina shift.

At the time of the experiment, the furnace is properly sealed and flushed with argon gas. The crucible containing fused melt is placed into the hot zone of the furnace. The refractory sample attached to the alumina shaft is suspended above the crucible. The furnace is programmed to reach the required temperature at a linear heating rate of 400 °C/h. After reaching the target temperature and the melt is in equilibrium, the refractory finger is slowly descended with certain rotation speed to submerge into the melt. The rotation speed is then adjusted to the required one. After the required reaction time at a given temperature and rotation speed, the refractory sample is raised rapidly to a temperature below 800 °C to stop the reaction, and the crucible with melt can be directly dropped into ice water.

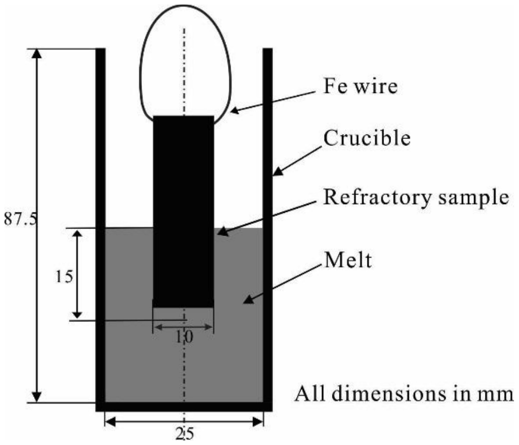

Fig. 2. Dimensions of the crucible and refractory sample used in high temperature corrosion test

Rapid cooling of the refractory and melt samples stops the high temperature reactions and the microstructure and compositions of the phases present in these samples are freezed. Analyses of the quenched samples will be able to provide accurate information at high temperature. The quenched refractory and melt samples are sectioned, mounted, polished and carbon coated for electron probe X-ray microanalysis (EPMA). The dimensions of the refractory samples were accurately measured and the penetration depth in the refractory can also be measured using optical microscope.

A commercial magnesia-chromite refractory sample (RF1), and a synthetic Fe_2O_3-Al_2O_3 material (RF2) were tested using the advanced corrosion test apparatus. The refractory corrosion status, phases present in the samples and their compositions measured by EPMA are discussed in this paper.

RESULTS

RF1: Commercial Magnesia-Chromite Refractory Sample

A commercial magnesia-chromite refractory sample was tested in an industrial copper smelting slag. The microstructure analysis of the refractory sample shows that it mainly consists of MgO phase with large $MgO.(Cr, Fe, Al)_2O_3$ spinel particles. MgO acts as the bonding phase which connects the spinel particles as an integrated structure. It is shown that this refractory has large pores present all over the sample. The number of pores can significantly affect the quality of the refractory, as the melts will infiltrate through the connected holes.

The refractory sample was cut and made to the cuboid shape as seen in Fig 2. The test was carried out with an industrial copper smelting slag held in a molybdenum crucible at 1250 °C in argon gas atmosphere. The composition of the copper smelting slag used for the test is shown in Tab. 1. The stability of the sample was tested at a relatively high rotation speed (40 RPM). During the rotation, the torques were monitored through the reading in the rheometer software. Effective torque values were seen for the first 100 minutes' rotation and then decrease to zero, which indicated that the rheometer was no longer linked to the refractory sample. The rheometer was raised and the crucible was directly quenched into water. Inspection of the remaining refractory sample hanged by the rheometer and the cross-section of the crucible shows that the refractory sample was corroded and broken inside the melt after 100 minutes rotation in the copper smelting slag.

The static corrosion test was also carried out for comparison purpose. The same refractory sample was immersed in the copper smelting slag (5-6 g) without rotation. In this experiment an alumina crucible (Φ14 mm and 40 mm height) was used instead of Mo crucible. After the reaction at 1250 °C for 120 minutes, the sample was quenched directly into the water. It was found that the sample after static corrosion test was kept its original shape. A dense layer of FeO.(Al,Fe)$_2$O$_3$ spinel was formed between the slag and alumina crucible.

Both samples were mounted and polished for EPMA analysis. The microstructures of the samples by the static test and rotational test are shown in Figs. 3 and 4 respectively. It can be seen from Fig. 3 that a clear solid layer was formed and covered the surface of the magnesia-chromite refractory material. The EPMA analysis shows that the newly formed solid layer is the (Fe^{2+},Mg)O.Fe$_2$O$_3$ spinel with limited dissolutions of ZnO, Cr$_2$O$_3$ and Al$_2$O$_3$ (composition refers to Tab. 1). The spinel layer stopped further reactions between the slag and the refractory material and well protected the refractory sample under static condition. It can be seen from Tab. 1 that some MgO from the refractory replaced FeO in the copper slag during the reaction. All Cr$_2$O$_3$ from the refractory was consumed to form new spinel and did not enter into the slag.

Table 1. Compositions of the copper smelting slag before and after the static corrosion test (wt%)

	FeO	SiO$_2$	Cu$_2$O	CaO	Al$_2$O$_3$	MgO	PbO	ZnO	Cr$_2$O$_3$
Slag before reaction	63.9	26.5	0.6	1.1	3.3	0.6	0.5	3.5	0
Slag after reaction	58.6	25.9	0.5	1.1	7.7	3.9	1.1	1.1	0
New spinel layer	83.2	0.3	0.1	0.1	1.7	10.4	0	0.9	3.3

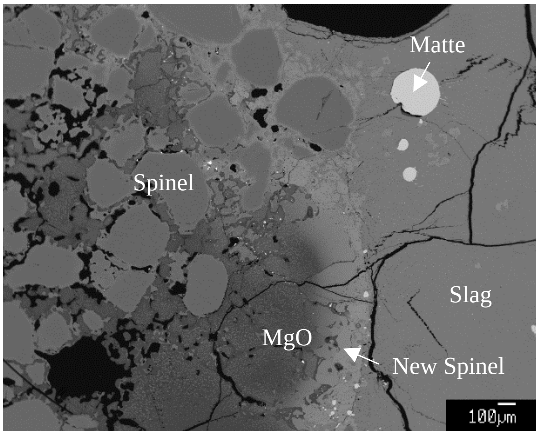

Fig. 3. Microstructure of the industrial magnesia-chromite refractory after the static test with copper smelting slag

However, under the dynamic test condition with a high rotational speed, the refractory structure was destroyed and the MgO.Cr$_2$O$_3$ spinel particles were separated by the olivine [2(Mg, Fe)O.SiO$_2$] phase as seen in Fig. 4. The compositions of the phases are given in Tab. 2. It can be seen from Fig. 4 that, without the protection of the spinel layer covering the sample, SiO$_2$ from the copper smelting slag continuously reacted with the MgO phase, which was the bonding phase in the refractory material, and formed the olivine phase. The MgO in the olivine phase can be substitute by the FeO from the copper smelting slag, which decreases the melting temperature of the olivine phase. Gradually, the olivine phase will be completely dissolved into the liquid slag. Under dynamic condition, the large spinel particles may then be washed away so that the refractory bricks will be peeled off by the liquid flow. At a high rotational speed, the reaction between the refractory and slag is very fast as demonstrated in the present experiment.

Table 2. Compositions of the phases present in the refractory after the rotation test (wt%)

	FeO	SiO$_2$	Cu$_2$O	CaO	Al$_2$O$_3$	MgO	ZnO	Cr$_2$O$_3$
Olivine	0.8	41.9	0.7	0.2	0	55.1	0.5	0.1
Spinel	8.5	0	1.1	0	15.8	20.6	3.7	49.9
MgO	3.5	0	0	0	0	96.5	0	0

Comparison of the experiments under static and dynamic conditions demonstrated that the physical wash by the melt plays an important role in the refractory degradations. Some of the materials may show a good resistance performance to the melt under the static condition. However, without a dense protective layer, the material may be deformed quickly under strong flow momentums. High-pressure gas injection in the furnace can create intense flow field so that a fast reaction rate between liquid and gas can be achieved. More and more copper smelting furnaces have been changed to the high-pressure gas injection through the tuyeres/lances. Under such intense circumstances, the stability of the magnesia-chromite refractory brick will face great challenges to the service life of the furnace lining. The present test is an important step for testing new refractories before they can be used in the industrial furnaces.

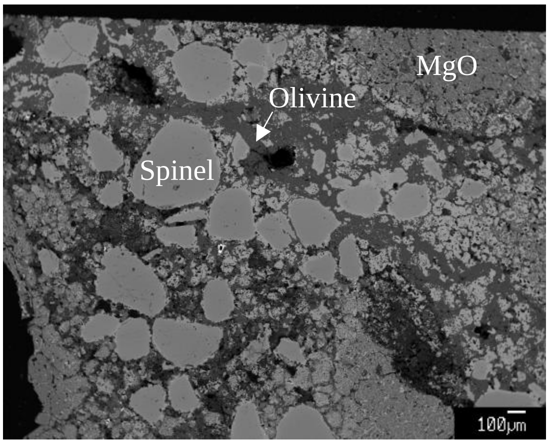

Fig. 4. Microstructure of the industrial magnesia-chromite refractory after the rotational tested in copper smelting slag

RF2: The Synthetic Fe$_2$O$_3$-Al$_2$O$_3$ Material

In copper making industry, despite the resistance to matte, the refractory should also have a good resistance to Cu$_2$O which is present in converting and refining slags [1-2]. The magnesia-chromite refractory has been proven to have little resistance to Cu$_2$O melt as the MgO bonding phase can react with Cu$_2$O so that the refractory structure will be completely destroyed.

In the present study, new corundum material in 8% Fe$_2$O$_3$-92% Al$_2$O$_3$ system was synthesized and tested for the Cu$_2$O-rich environment in copper making industry. The phase equilibrium study in the Cu$_2$O-Al$_2$O$_3$ system indicates that both of the solubilities of Cu$_2$O in Al$_2$O$_3$ and Al$_2$O$_3$ in Cu$_2$O are limited [6]. It was speculated that the corundum material may have a good resistance to the Cu$_2$O melt. The microstructure of the synthetic corundum sample prepared at 1700 °C in air is shown in Fig. 5. The microstructure shows that the material consists of corundum as the predominant phase with small amount of Fe$_3$O$_4$ present. Approximately 7 wt% Fe$_2$O$_3$ was dissolved into the corundum phase. It can be seen from Fig. 5 that the pores present in this material are isolated and smaller compared to the industrial magnesia-chromite refractory shown in Fig. 3.

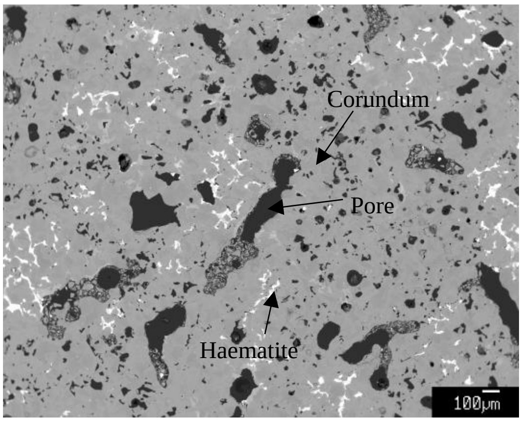

Fig. 5. Microstructure of the synthetic Fe_2O_3-Al_2O_3 material prepared at 1700 °C in air

The corundum material was shaped and tested using the rotational corrosion test apparatus. The material finger was rotated at a speed 20 RPM in the Cu_2O melt held in alumina crucible at 1300 °C. After 2 hours rotation, the material finger was ascended to the cold zone and the melt was directly quenched into water. After cooling down to room temperature, the refractory sample was taken out and the dimension of the sample was measured. Comparison of the measurements before and after the test shows that the dimensional change was very small (less than 0.5 mm) after rotation in Cu_2O melt for 2 hours.

The corundum material and the Cu_2O after the test were mounted and analysed by EPMA. The microstructure of the interface between the refractory and Cu_2O is shown in Fig. 6. It can be seen that, a solid delafossite layer (20 µm thick, 57.2 wt% Cu_2O-40.8 wt% Al_2O_3-2.0 w% Fe_2O_3) was formed and covered the corundum material. The EPMA analysis of the quenched sample shows that limited Al_2O_3 was dissolved in the Cu_2O melt and no delafossite crystal was present in the melt. The microstructural and compositional analyses indicate that the delafossite layer was firmly formed at the interface between the refractory sample and the melt and stopped the further reaction. At rotation speed 20 RPM for 2 hours, the solid delafossite layer did not detach from the refractory.

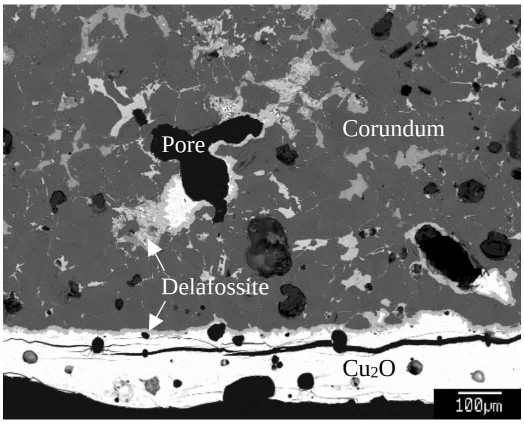

Fig. 6. Microstructure of the synthetic Fe_2O_3-Al_2O_3 material after the rotational test in the Cu_2O melt

It seems that the Fe_2O_3-Al_2O_3 corundum material shows good resistances in both physical wear under shear stress and chemical corrosion by the Cu_2O melt at high temperature. This material has the potential to be used in the area containing high Cu_2O.

CONCLUSIONS

In the present study, an advanced corrosion test apparatus has been developed. The apparatus rotates the refractory sample inside the liquid to simulate the physical wear inside the high temperature bath. The apparatus also has the features including wide adaptability to the different melts, gas-tight to simulate different oxygen partial pressures and fast-cooling of the refectory sample and melt. These features enable the physical wear and chemical corrosion of the refractory sample to be investigated closely to the industrial operating conditions.

A commercial magnesia-chromite refractory sample and synthetic Fe_2O_3-Al_2O_3 corundum material were tested using the advanced apparatus with copper smelting slag and Cu_2O melt respectively. The industrial magnesia-chromite refractory sample tested at a high rotation speed was destroyed completely without the formation of solid layer at the interface, which was formed in the static corrosion test. The tests demonstrated that physical wear plays a significant effect in the refractory corrosion. The Fe_2O_3-Al_2O_3 corundum material shows a good corrosion resistance to the Cu_2O melt and no dimensional changes with rotations, which shows the potential to be used in the areas in contact with melt containing high Cu_2O.

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REFERENCES

1. Schlesinger ME, Davenport WG, Sole KC, King MJ. Extractive Metallurgy of Copper. 5th ed. Oxford: UK; 2011.
2. Malfliet A, Lotfian S, Scheunis L, Petkov V, Pandelaers L, Jones PT, Blanpain B, Degradation mechanisms and use of refractory linings in copper production processes: a critical review. J Eur Ceram Soc. 2014; 34(3):849–876.
3. Crites MD, Karakus M, Schlesinger ME, Somerville M, Sun S, Interaction of chrome-free refractories with copper smelting and converting slags. Can Metall Q. 2000; 39(2):129-134.
4. Zhao B, Cui Z, Wang Z. A new copper smelting technology: bottom blown oxygen furnace developed at Dongying Fangyuan Nonferrous Metals. In: Jiang T, Hwang JY, Mackey PJ, Yucel O, Zhou GF, editors. TMS 2013: Proceedings of the 4th International Symposium on High-Temperature Metallurgical Processing; 2013 Mar 3-10; San Antonio, United States. Hoboken: John Wiley & Sons; 2013. p. 3-10.
5. Cui Z, Wang Z, Wang H, Wei C. Two-step copper smelting process at Dongying Fangyuan. In: Copper 2016: Proceedings of Copper 2016; 2016 Nov 13-16; Kobe, Japan. 2016. PY16-4.
6. Chen M, Zhao B. Phase equilibrium studies of ‘Cu_2O’-SiO_2-Al_2O_3 system in equilibrium with metallic copper. J Am Ceram Soc. 2013; 96(11):3631-6.