A STUDY ON KINETICS OF SLAG CORROSION OF ALUMINA REFRACTORY

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ABSTRACT

The service life of high temperature metallurgical furnace, such as blast furnace, depends largely on the life of its refractory line, which is mainly determined by the corrosion of the slag. In order to investigate the slag corrosion mechanism and the real corrosion rate as the corrosion process goes on. A new slag corrosion method has been designed in the present paper. The relationship between the slag viscosity and the corrosion depth of the refractory rod was established. The slag corrosion rate can be determined by measuring the changes of slag viscosity. Blast furnace slag corrosion experiments of alumina refractory, at different temperature and time, have been carried out. The corrosion rate is increases as the temperature increases, while it is decrease as the corrosion process goes on. The corrosion rate on the whole process was determined with the measurement of the slag viscosity. The most advantage of this method is that the slag corrosion rate can be determined at any time during the process. Therefore, the corrosion with the initial slag, which is important, could be calculated. The slag corrosion kinetics has been experimental studied and the activation energy of BF slag corrosion on the prepared high alumina refractory is 308.7 kJ/mol.

Key Words: Slag corrosion; BF slag; Alumina refractory; Viscosity.

INTRODUCTION

Alumina refractory is widely used as lining materials in high temperature metallurgical furnace, such as BF furnace. The service life of BF Furnace depends largely on the life of its alumina refractory line which is mainly affected by the corrosion of the slag. Therefore, a number of scientists have paid attention on the experiments of the slag corrosion and the corrosion mechanism [1, 2, 3]. Several corrosion methods were used in refractory-slag corrosion experiments. Those methods are usually divided into two kinds, one is the static state corrosion experiment and the other is the dynamic corrosion experiment. During the static state corrosion experiment [3, 4, 5], the prepared refractory cylinder (or rectangular) was put into the slag melts or the liquid slag was put into refractory crucible at certain temperature. After certain time interval, the experiment was stopped, and the corrosion depth will be measured to determine the corrosion rate. During the dynamic corrosion experiment, the crucible or the cylinder refractory sample was controlled to be rotated, or the slag was controlled dropping to the refractory surface constantly [6, 7].

The static slag corrosion experiment is easy to carry out, but quite different from the real corrosion condition. The dynamic corrosion experiments have drawn the attention of people because it increases the movement between the refractory and the slag. It would be a little similar to the real slag corrosion condition. However, it is also difficult to simulate the real corrosion process for the following reasons. In the real slag corrosion process in BF furnace, composition of slag in some certain place will be renewed all the time. While, in the slag corrosion experiment, the composition of slag will be changed as the corrosion process goes on. As the composition changes, the corrosion rate will also changes. The experiment could only get an average corrosion rate. On the other hand, the real corrosion rate will be equal to the initial corrosion rate of the experiment.

In order to investigate the slag corrosion mechanism and the real corrosion rate as the corrosion process goes on. A new slag corrosion method has been designed in the present paper. The slag corrosion rate can be determined by measuring the changes of slag viscosity. And the relationship between the slag viscosity and the corrosion rate was established. The corrosion experiments of the synthesis BF slag and the high alumina refractory have been carried out and the corrosion kinetics have been discussed.

METHODOLOGY

The corrosion experiment was carried out in a rotational viscometer, as shown in Figure1. In viscometer, there are two different radius concentric circularities, on the inner and out surface of the slag, respectively. Outside circularity is the molybdenum crucible and the inner side is a molybdenum cylinder (probe). Liquid slag was filled between the two circularities. As the inner cylinder was forced to rotate, then the velocity grads will be produced along the radial direction across the slag. The inner friction force will be produced between the slag layers. A tangent direction stress will be produced because of the friction force. The viscosity (η) will be measured by measuring the stress.

In the present paper, the refractory sample was prepared as a cylinder of ϕ20.4*55 mm3. The refractory cylinder was acted as the inner cylinder (or probe) in the rotational viscometer system. The slag was put in the molybdenum crucible and the experimental temperatures were controlled to be 1723 K-1823 K. As the corrosion process goes on, the refractory probe (cylinder specimen) will be dissolved into the slag. As the dissolving continues, the composition of the slag will be changed. Meanwhile, the viscosity of the slag will be changed and the diameter of the inner refractory cylinder will be reduced as well. Therefore, the diameter changes will be related to the changes of slag viscosity. The corrosion rate (the diameter changing rate) can be measured by measuring the slag viscosity.

Suppose the radius of the inner refractory (the probe) is r, the inner radius of the crucible is R, the immerging depth of the probe is h and the rotation speed is ω. The rotation moment by the inner friction force of the slag can be deduced as Equation 1.

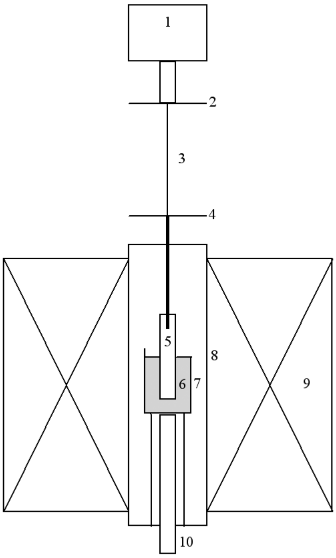

Figure1: The sketch of slag corrosion experimental apparatus. 1) Electric motor; 2) Up disc; 3) Pendent wire; 4) Lower disc; 5) Refractory specimen; 6) Liquid slag; 7) Crucible; 8) Tube; 9) Heat furnace; 10) Thermocouple

$$M = 4\pi\eta h\omega / (1/r^2 - 1 / R^2) \qquad (1)$$

A metallic wire was fixed between molybdenum rod and the motor. The rotation force moment will act on the wire and make it torsion. The twist moment can be deduced as:

$$M_t = \varphi\,(G \cdot J_p / l) \qquad (2)$$

In Equation 2, φ is the angle of torsion; G is elastic coefficient of the wire; J_P is inertia moment of the wire; l is the length of the wire.

When the measuring system is in a steady state, $M=M_t$, then:

$$\eta = \varphi \cdot G \cdot J_p \cdot (1/r^2 - 1 / R^2) / 4\pi\eta h \cdot \omega \cdot l \qquad (3)$$

As $\varphi/\omega = \Delta t$ and Δt is the rotation time difference between the up and low end of the wire because of the torsion.

Let $(G \cdot J_p) / (4\pi h \cdot l) = k$, then:

$$\eta = k \cdot (1/r^2 - 1 / R^2) \cdot \Delta t \qquad (4)$$

In common slag viscosity measuring process, r and R are constant (known). k can be determined from the standard solution with known viscosity. Therefore, the slag viscosity (η) can be measured by the measuring the rotation time difference (Δt). Δt can be sensed with optic time-meter from the up and low disc gaging hole. In fact, the measured

$\Delta t_m = \Delta t_0 + \Delta t$, Δt_0 is produced by the measuring system rotating in the air, and Δt is produced by the slag viscous force. Δt_0 can be calibrated with the standard solution.

In the present experiment, the inner cylinder was made of high alumina refractory, not of molybdenum. The refractory cylinder will be dissolved into the slag gradually during measuring process. Then the radius of the cylinder will be decreased gradually during the process. On the other hand, when the refractory cylinder was dissolved into the slag, the composition of the slag will be changed gradually. And the viscosity of the slag will be changed as well. The viscosity change is related to the composition change and to the amount of dissolved refractory. Suppose the refractory was dissolved evenly on the surface. Then the amount of dissolved refractory is related to the decrease of the radius of the cylinder (or the corrosion depth). Then the slag viscosity was related to the changes of the radius (or the corrosion depth) of the refractory probe. At fixed condition (same initial composition and amount of slag, same composition and size of refractory cylinder and same temperature), the relationship between the viscosity and the radius can be experimental determined by adding some refractory to the slag: $\eta = \eta(r)$. Then the following equation can be obtained.

$$\eta\ (r) = k \cdot (1/r^2 - 1\ /\ R^2) \cdot \Delta t \tag{5}$$

k can be determined by the standard solution with known viscosity, R is constant. $\eta(r)$ is an expression of variable r. Therefore, Equation (5) is a relation of r and Δt. Then, r can be calculated by measuring Δt. The corrosion depth can be obtained.

In the present paper, the composition of the refractory probe is CaO: 1.1%, SiO_2: 12.0%, Al_2O_3:85.1%, FeO: 0.4%, other elements: 1.4%. The raw material (power) was pressed into a rectangular and baked at 1873 K for 3 hours. The refractory probe was shaped, with a drill, in a rod of $\phi 20.\tilde{4} \times 55$ mm with a hole on the top for fixing it on the measuring rod. The density of refractory is 2.3 g/cm^3 and the porosity is 20.1%. The slag is an artificial synthesis one with the composition of CaO: 40%, SiO_2: 37%, Al_2O_3:13%, MgO: 7%, TiO_2: 3%.

RESULTS AND DISCUSSION

150 g synthesis slag was put into the molybdenum crucible in the furnace and heated at 1723 K, 1773 K and 1823 K respectively. At the first step, the inner cylinder was the standard molybdenum probe. The different amount of refractory was added to the slag, the supposed corresponding corrosion depth of the refractory cylinder can be calculated from its density (2.3 g/mm^3) and the immerging depth (30 mm). The slag viscosity at different temperature can be measured and it is shown in Table 1. And the relationship of η and corrosion depth Δr at different T can be obtained.

Table 1: Slag viscosity with different amount refractory addition at different T

No.	Δm g	R mm	η (1723K) Pa·S	η (1773K) Pa·S	η (1823K) Pa·S
1	0	10.2	0.612	0.478	0.439
2	2.99	9.5	0.883	0.593	0.531
3	6.89	8.5	1.274	0.961	0.827
4	11.92	7	1.807	1.489	1.299
5	17.12	5	2.935	2.325	1.902

The relationship of slag viscosity (η) and the refractory cylinder radius r at 1723 K, 1773 K and 1823 K can be regressed as shown in Equation 6 - Equation 8 (the unit of radius r is mm)

$$\eta = 6.52 - 0.86\,r + 0.028\,r^2\ (\mathrm{Pa{\cdot}S}) \qquad T=1773\ \mathrm{K} \qquad (R=0.998) \tag{6}$$

$$\eta = 5.15 - 0.66\,r + 0.022\,r^2\ (\mathrm{Pa{\cdot}S}) \qquad T=1773\ \mathrm{K} \qquad (R=0.999) \tag{7}$$

$$\eta = 3.88 - 0.44\,r + 0.010\,r^2\ (\mathrm{Pa{\cdot}S}) \qquad T=1773\ \mathrm{K} \qquad (R=0.997) \tag{8}$$

After determination of the relationship of η and r, the corrosion experimental at different T was carried out with the synthesis slag. The Δr can be calculated by the measured Δt with the determined relationship of η and r at different T. Combination of Equations (6-8) and Equation (5), the relationships of r and Δt at 1723 K, 1773 K and 1823 K are as follows:

$$6.52 - 0.86\,r + 0.028\,r^2 = \mathrm{k} \cdot (1/r^2 - 1\,/\,R^2) \cdot \Delta \mathrm{t} \tag{9}$$

$$5.15 - 0.66\,r + 0.022\,r^2 = \mathrm{k} \cdot (1/r^2 - 1\,/\,R^2) \cdot \Delta \mathrm{t} \tag{10}$$

$$3.88 - 0.44\,r + 0.010\,r^2 = \mathrm{k} \cdot (1/r^2 - 1\,/\,R^2) \cdot \Delta \mathrm{t} \tag{11}$$

In Equations (9-11), k can be determined by the standard solution and R is constant. Then the refractory probe radius r (and the corrosion depth Δr) can be calculated from the measured time difference Δt at given temperature. The slag corrosion results at different corrosion time are shown in Figure 2.

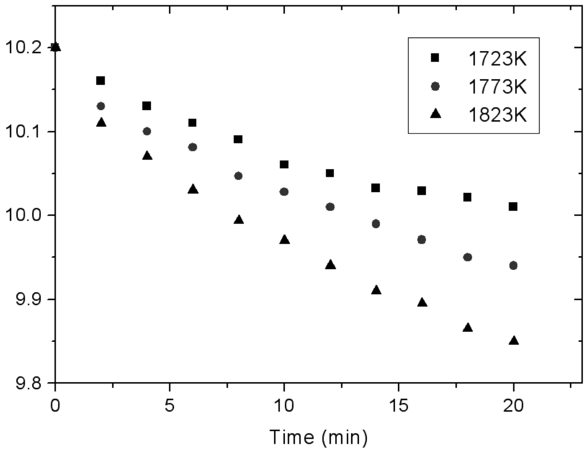

Figure 2: The experimental results of slag corrosion

As can be seen from Figure 2, the slag corrosion rate is increased as the corrosion temperature increases. The main reason is that the viscosity of slag decreases as T increases and the diffusion is easier. Therefore, in BF furnace, the strong shell cooling system along the lower part of BF shaft will improve the lining resistance to slag corrosion. As also can be seen from Figure 2, the slag corrosion rate is decreased as the corrosion process goes on. The main reasons are as follows. As the corrosion process goes on, the refractory will be dissolved into the slag, the viscosity of slag will be increases which will degrade the corrosion kinetic condition. On the other hand, as the refractory composition dissolved into the slag, the dissolve thermodynamic condition will be degraded as well.

It can be seen from Figure 2, the initial corrosion rate could be obtained from the slope of the curve and the initial corrosion rate is obviously the fastest at a given temperature.

At each temperature, the square of the corrosion depth Δr is linear ratio to the corrosion time t. ($\Delta r^2=kt$). The results are shown in Figure 3. Therefore, the diffusion might be the process rate controlling step.

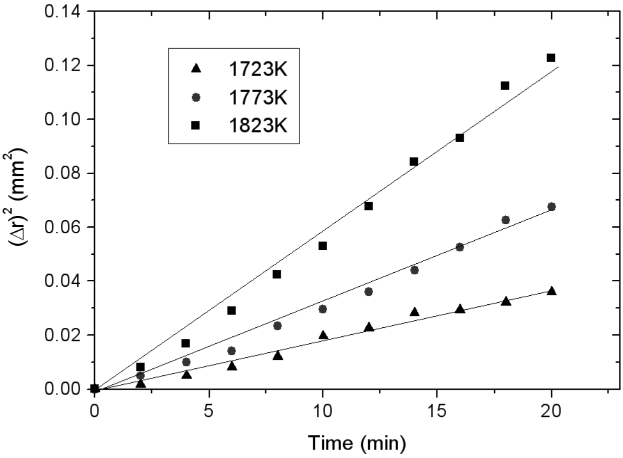

Figure 3: Relation of the corrosion time and the square of the corrosion depth

The corrosion rate constant k can be obtained from Figure 3. According to Arrenius equation, the relation of corrosion rate constant k and corrosion temperature T are shown in Figure 4. The overall corrosion activation energy E can be calculated, which is 308.7 kJ/mole. The large activation energy indicated that the corrosion mechanism might be quite complicated.

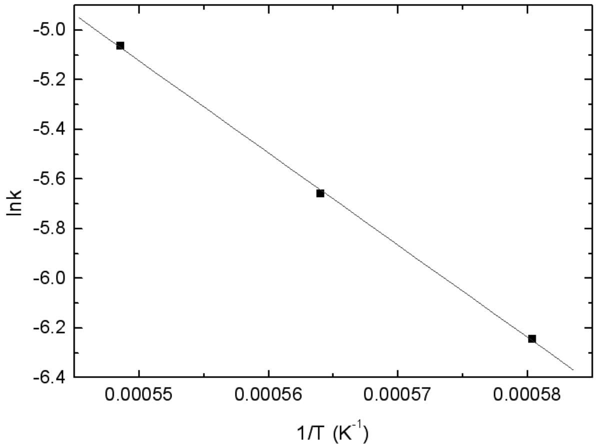

Figure 4: Relation of ln(k) and 1/T of the slag corrosion

The main advantage of the present corrosion method is that the corrosion rate can be obtained at different process time. Especially, the corrosion rate at the initial stage of corrosion can be obtained. The initial corrosion rate is very important which would be the real corrosion rate as the slag composition is the designed one. The disadvantage of the present method is that the corrosion process is a little complicated. The equation of $\eta = \eta(r)$ should be calibrated before corrosion experiment and the refractory specimen should be prepared into a cylinder as the probe.

In the present method, some error may be generated as several assumptions were included. The corrosion rate was considered as an even corrosion on the surface of the probe and the slag composition was considered as homogeneous. And the bottom effect of the probe was neglected.

The present method can be extended to the other kind of refractory and other slag.

CONCLUSIONS

At the present paper, a new slag corrosion experimental method has been established by deducing a relationship of the corrosion depth and the viscosity of slag.

The corrosion experiments have been carried out at different temperatures. The experimental results show that the slag corrosion rate is increased as the corrosion temperature increases and the slag corrosion rate is decreased as the corrosion process goes on.

The main advantage of the present corrosion method is that the corrosion rate can be obtained at different process time. Especially, the corrosion rate at the initial corrosion time can be obtained. The initial corrosion rate is very important which would be the real corrosion rate as the slag composition is the designed one. The disadvantage of the present method is that the corrosion process is a little complicated. The equation of $\eta = \eta(r)$ should be calibrated before corrosion experiment and the refractory specimen should be prepared into a cylinder as the probe.

The slag corrosion kinetics has been discussed and the overall corrosion activation energy E is 308.7 kJ/mole.

The present method of slag corrosion can be extended to the other kind of refractory and other slag.

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