

MECHANISM OF CORROSION OF MAGNESIA-CARBON REFRACTORIES IN SLAGS CONTAINING IRON OXIDE

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Abstract

Measurement of rate of corrosion of MgO-C refractories have been made by a rotating method with cylindrical specimens containing 4.8 and 13.0 mass % graphite in slags which contained MgO up to 6.0 mass% at 1673K. The rate of the corrosion of the refractory decreased in case of smaller content of graphite in the refractory and with increasing of MgO contents in the slag. The corrosion of the matrix proceeded faster than that of the coarse periclase. It is speculated that the corrosion process was mainly controlled by the dissolution of the periclase in the slag, and the dissolution of the periclase was accelerated by the agitation of the CO bubbles produced by graphite oxidation.

Introduction

Improvement of corrosion resistance of magnesia-carbon refractory that is used as lining of ladle for hot metal pretreatment or of converter for steel refining contributes to making high quality steel. Cause of corrosion of the refractory in operation on steel making is very complex. Clarification of the corrosion mechanism of the refractory is available for the design for the linings with suitable performance for the steel making vessels. The oxidation of the graphite by FeO and the dissolution of MgO in the slag affect the corrosion behavior of MgO-C refractory in the molten slag. The dissolution mechanism of a sintered magnesia rod ^{(1),(2)}, or of a crystal magnesia in the slag has been reported ⁽³⁾, the corrosion rate of the MgO-C refractory decreased when the content of FeO in the slag and of graphite in the refractory decreased ^{(4),(5)}. On the other hand, the rate of local corrosion of the refractory with 25 mass % graphite was smaller than that of the refractory with 15 mass % graphite ⁽⁶⁾. The mechanism of corrosion of MgO-C refractory has not been clarified sufficiently. In the present study, the effect of the FeO or MgO contents in the slag and C content in the refractory on the corrosion rate has been investigated.

Experiment

The present experiment was carried out by a rotating immersion method using a cylindrical specimen. The compositions of the MgO-C refractory were listed in table 1. Electro-fused magnesia and natural flake graphite were kneaded with addition of binder, and were pressed into a shaped brick. The cylindrical specimen of 25 mm in diameter and 30 mm in height was cut from the brick or the sintered magnesia brick with a diamond core drill and a diamond saw. The specimen mounted between iron caps with iron shaft in 6 mm diameter was preheated to decompose the binder and to prevent thermal shock. After being preheated, the specimen was immersed into the molten slag, and it was run at 50 rpm for 20 minutes at 1473K and 1523K. The slag weighing 666g was melted in an iron crucible. Table 2 shows the slag compositions. The slag basicity was 1.2. A small amount of slags were sampled with a copper rod at 4 minutes intervals until 20 minutes passed to measure the amount of magnesia dissolved in the slag. The decrease of the radius of the specimen was determined by calculating the amount of dissolved MgO in the slag. Furthermore the diameter of the specimen after the corrosion test was measured with a slide caliper.

Result and Discussion

The corrosion of the matrix of the refractory in the slag containing FeO was faster than that of the periclase. Fig. 1 shows the time dependence of the radius of the MgO-C refractories in the slag containing FeO or no FeO, and that of the sintered MgO in the slag containing FeO.

Relationships between the decrease of the radius and the immersion time were linear. The rate of the corrosion was defined by the slope of the straight line. The rate of the corrosion of the MgO-C refractory in the slag with 15 mass % FeO was larger than that in the slag with no FeO. The rate of the corrosion of the MgO-C refractory in case of no oxidation of C was almost the same with that of the sintered MgO. It suggests that the rate of the wear of the matrix is proportional to that of the oxidation of C by equation (1)



. It was reported that rate of oxidation of the graphite rod by molten slag containing FeO was proportional to the activity of FeO by previous researchers ^{(7) (8)}. Fig. 2 shows the relation between the rate of corrosion of MgO-C refractories and the contents of FeO in the slag. The rate of the corrosion was increased with increasing of the FeO contents in the slag. The wear of the matrix affects the corrosion of the refractory strongly. Penetration velocity of slag into porous MgO refractory was very large by slag penetration test ⁽⁹⁾. In the same way molten slag penetrates rapidly into the pores in the decarburized layer which was formed by the oxidation of C in the matrix. The periclase dissolved in the slag penetrated into the pores. Fig. 3 shows the relation between the decrease of the radius and the immersion time for the MgO-C refractory with 4.8 and 13.0 mass % C. The rate of the corrosion in case of 13 mass % content of C was much larger than that in case of 4.8 mass % C. It suggests that the rate of the corrosion increases with increasing of the pores in the decarburized layer formed by the wear of the matrix. The diameter of the pores enlarges after the dissolving of the periclases in the slag penetrated into the pores. The relation between the rate of the corrosion and the MgO contents in the slag was shown in Fig 4. The rate of the corrosion decreased with increasing of the MgO contents in the slag. The rate of the corrosion was negligible in the slag with 6.5 mass % MgO contents, which was the saturated content of MgO. The dissolution of the periclases in the slag penetrated into the pores does not occur in case of the slag saturated of MgO, so the diameter of the pores maintains the initial small size. It was speculated that the contact of the graphite with the penetrated slag was prevented by the CO gas that filled in the pores with small size of the diameter. As shown in Fig. 1, the rate of the corrosion of the MgO-C refractory was much large in comparison with that of the sintered MgO in the slag containing FeO and no MgO. Furthermore, the decreasing of the rate of corrosion was proportional to the MgO content in the slag as shown in Fig.4. On the assumption that mass transfer in the laminar film controls the dissolution process of the solid MgO in the slag, the dissolution rate is represented by the equation (2).

$$-dr/dt = k\rho_b/(100\rho)\Delta(\text{mass \% MgO}) \quad (2)$$

k: mass transfer coefficient (cm/sec), ρ_b : density of the bulk slag (g/cm³), ρ : density of the solid specimen (g/cm³), $\Delta(\text{mass \% MgO})$: difference between MgO concentration in the bulk slag and the saturated concentration of MgO on the surface of the solid MgO.

It is known that mass transfer coefficient follows the Arrhenius' type temperature dependence in equation (3).

$$k = A \exp(-E_k / RT) \quad (3)$$

A: constant, E_k : apparent activation energy (J/mol), R: gas constant, T: temperature

Being taken logarithms of the left hand term and right hand term in equation (2), $\ln(-dr/dt)$ is proportional to the $\ln k$. Consequently $\ln(-dr/dt)$ is proportional to $-E_k / RT$. Fig.5 shows the effect of temperature on the corrosion rate of the MgO-C refractories with no MgO and 15 mass % FeO content, and with 3 mass % MgO and 7 mass % FeO content. The relation between the reciprocal temperature and the corrosion rate showed almost the linearity. The apparent activation energy was 166 kJ/mol or 160 kJ/mol respectively, which was almost similar with the activation energy, 147 kJ/mol, obtained by the kinetic study of the dissolution of the sintered MgO(1) It suggests that the controlling step of the corrosion process of MgO-C refractory was the same with that of sintered MgO, and the corrosion of MgO-C refractory

is promoted because of the slag agitation by the fine CO bubbles floating up in the boundary layer.

Conclusion

As the result of the corrosion test of MgO-C refractory in the slag containing FeO or MgO, the mechanism of corrosion was suggested as follows. The slag penetrated into the pores contacts with the graphite in the matrix, and then CO gas produces as the result of chemical reaction of C with FeO in the slag. The diameter of pores is enlarged because the periclases dissolve in the penetrated slag, so CO gas goes out through the pores easily. It was speculated that the dissolution of MgO-C refractory was mainly controlled by mass transfer in the boundary layer.

Reference

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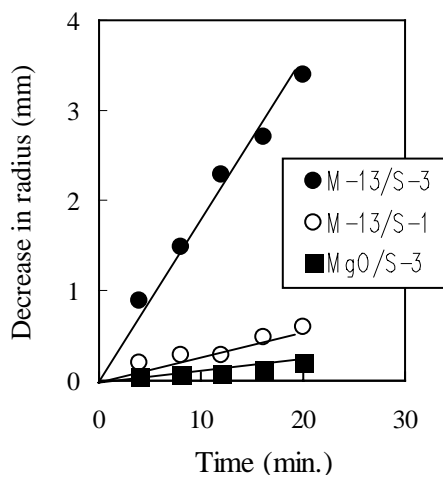


Fig.1 Effect of oxidation of graphite in the refractories on decrease in the radius.

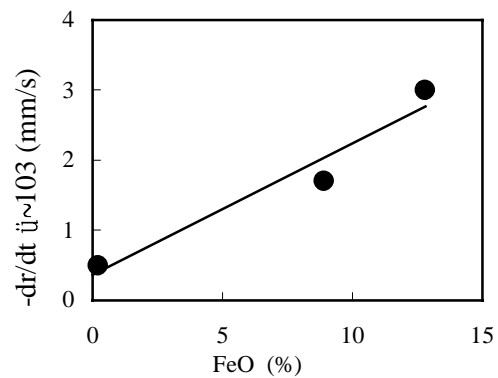


Fig. 2. Relation between rate of decrease of the radius and FeO contents in slag.

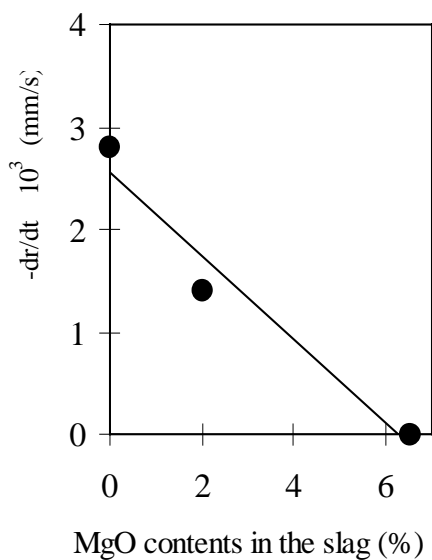


Fig. 4. Relation between the decrease of the radius and MgO contents in the slag.

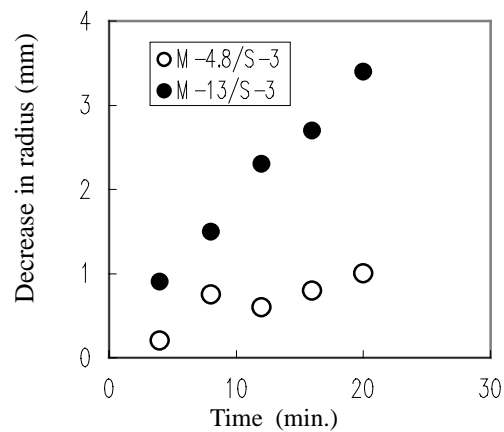


Fig. 3. Effect of the graphite contents in the refractories on the decrease of the

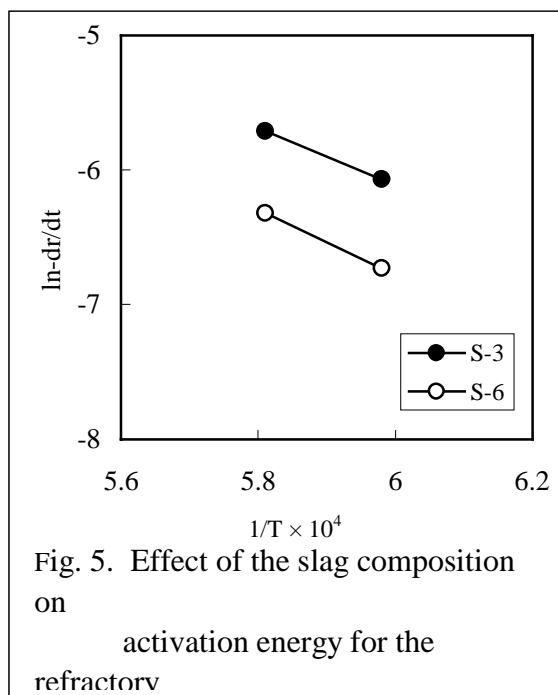


Table 1. Compositions of MgO-C refractories. (mass %)

Slag	CaO	SiO ₂	FeO	CaF ₂	MgO
S-1	40.0	34.9	0	25.0	0
S-2	49.3	42.5	8.9	4.1	0
S-3	44.6	37.5	15.0	4.0	0
S-5	44.0	37.9	12.0	4.1	2.0
S-6	46.0	40.0	7.0	4.0	3.0
S-7	40.5	35.0	13.6	4.2	6.7

Table 2. Chemical compositions of slags. (mass %)

Specimens	Magnesia	Graphite	Binder
M-4.8	95.2	4.8	2.2 (addi.)
M-13	87.0	13.0	2.8 (addi.)
Specimens	Magnesia	Graphite	Binder
M-4.8	95.2	4.8	2.2 (addi.)
M-13	87.0	13.0	2.8 (addi.)