## Oxidation Rate Of Magnesia-Carbon Refractory Under Low Oxygen Partial Pressure

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Decarburization of resin-bonded magnesia-carbon refractory, as one of important materials of lining of vessels used on steel making process, has been investigated kinetically in the temperature range from 1473 to 1673 K in N<sub>2</sub>-O<sub>2</sub> and Ar-O<sub>2</sub> mixed gas with 2.1  $\times$  10<sup>4</sup> and 3.7  $\times$  10<sup>2</sup> Pa in oxygen partial pressure respectively.

Coarse and fine sintered sea water magnesia grains, natural flake graphite and phenol resin were kneaded and were compacted into a shaped brick. The graphite content in the brick was 5 mass %. Phenol resin of 2.0 mass % was added as the carbon binder. A cubic specimen with sides 20mm long each placed in a basket was suspended in an electric resistance furnace. The oxygen partial pressure was monitored with a magnesia stabilized zirconia solid concentration cell. The decrease of weight loss of the specimen was measured with a thermobalance. Fig.1 shows the variation of the oxidation rate with temperature as a function of oxidation time in Ar-O<sub>2</sub> and  $N_2$ - $O_2$ . First the oxidation test under  $3.7 \times 10^2$  Pa in oxygen partial pressure was conducted for 300 minutes, and then Ar-O\_2 atmospheric gas was changed for  $N_2\text{-}O_2$ mixed gas with  $2.1 \times 10^4$  Pa in oxygen partial pressure. The chemical reaction of the C burnout in magnesiacarbon refractory is expressed by equation (1). The oxidation under lower oxygen partial pressure was slower than higher oxygen partial pressure.

$$2C(s) + O_2(g) = 2CO(g)$$
 (1)

It was suggested that the recession velocity of the interface of graphite phase decreased with decreasing of oxygen partial pressure in atmospheric gas. When oxidation temperature increased up to 1673 K, the oxidation rate decreased abruptly as shown in Fig. 1.

The specimen, which was not oxidized perfectly, was pulled up from the furnace and cooled. The cross section of the specimen was observed. The boundary between decarburized layer and undecarburized layer was clear. Topo-chemcal reaction model was applied to the oxidation model to analyze the oxidation process. The mathematical model regarding topo-chemical reaction model includes the terms of mass transfer resistance through boundary layer in gas phase, diffusion resistance through porous decarburized layer and chemical reaction resistance at the interface between decarburized and undecarburized layer. After kinetic analysis, it was speculated that the over all oxidation process was controlled by the diffusion of  $O_2$  through the porous decarburized layer.

The effective diffusion coefficients of  $O_2$  were obtained by analysis of the oxidation process. Fig 2 shows Arrhenius plots of the effective diffusion coefficient,  $D_e$ . The activation energies obtained in the oxidation test were 36 and 37 kJ per mol. The value of  $D_e$  obtained from the oxidation test in Ar-O<sub>2</sub> atmospheric gas decreased abruptly when the oxidation temperature increased up to 1573 K as shown in Fig.2. The confirmation of dense layer formation on the surface of the specimen was achieved by the observation of the cross section of specimen after the oxidation test in  $Ar-O_2$ . The formation of dense layer is expressed by equation (2) and (3).

$$MgO(s) + C(s) = Mg(g)$$
<sup>(2)</sup>

$$2Mg(g) + O_2(g) = 2MgO(s) + CO(g)$$
 (3)

Magnesium vapor generated by the reaction (2) diffused through the pores in the decarburized layer toward the surface, and reacted with  $O_2$  invaded from the surface to graphite phase to form MgO expressed in equation (3). The value of partial pressure of  $O_2$  in the vicinity of the interface between decarburized layer and graphite phase was almost the same as the one in equation (3). Secondary periclase (MgO) condensed on the inner wall of pores and piled there. Recession speed of graphite phase was slow under low partial pressure of oxygen, so the dense layer formed near the surface.

The dense layer formation is available for decreasing wear of MgO-C lining of vessels used on steel making process.



Fig.1 Effect of temperature on the oxidation rate in atmosphere with oxygen partial pressure of  $3.7 \times 10^2$  Pa and  $2.1 \times 10^4$  Pa.



Fig.2 Arrhenius plots of the effective diffusivity De.