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The Mechanism of the Reduction of Hematite-Magnetite Concentrate by Graphite-Calcium Carbonate Mixture in Hoganas Process

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1. Introduction

Tunnel kiln sponge iron production process has some advantages over other coal-based processes including lower initial investment, ease of implementation and scalability. One main drawback of this process is the long process time and consequently excessive energy consumption, and therefore, more research has to be conducted to improve the energy efficiency and the productivity.

Several studies have explored the mechanism of iron oxide reduction in coal-based processes. The importance of carbon gasification by CO_2, heat conduction and gaseous diffusion in the pellets was mentioned in these investigations.

There are not many scientific publications addressing the role of heat and mass transfer in the reduction of iron oxide in this process. The experimental conditions in these studies are such that the results do not provide a good interpretation from the effects of heat and mass transfer on the reduction of iron oxide in tunnel kiln.

In this study, the mechanism of the reduction of hematite-magnetite concentrate in the form of a hollow cylindrical pellet in Hoganas process has been investigated using graphite-calcium carbonate mixture as the reductant.

2. Experimental

Hematite-magnetic concentrate (HMC) obtained from Golgohar Mining and Industrial Co., was used as iron oxide source (Table I). A mixture of graphite (Table II) with calcium carbonate (Table III) at a ratio of 5 to 1 was used as the reductant.

Table 1. Chemical Composition of Hematite-Magnetite Concentrate (HMC) (wt %)

Total Fe	FeO	SiO_2	CaO	Al_2O_3	MgO	SO_3	LOI
65.73	7.95	1.81	1.02	0.26	1.02	0.33	0.95

Table 2. Proximate Analysis of the Graphite (wt %)

FC	VM	Ash	Moisture
89.28	7.69	1.69	1.34

Table 3. Chemical Composition of Calcium Carbonate (wt %)

CaO	MgO	Fe_2O_3	SiO_2	Na_2O	SO_3	LOI
44.04	7.41	1.79	3.68	0.32	0.6	40.82

The HMC samples were prepared as a hollow cylinder by adding water and sodium bentonite to reach the appropriate strength. The sample was dried in two steps: 75 min at 110 °C and 90 min at 160 °C.

A heat resistant steel (A310) crucible was used. Two holes were arranged on the cap of the crucible to place the thermocouples inside the reductant mixture (Figure 1). The HMC sample was placed inside the crucible and the crucible was filled by the reductant mixture, as shown in Figure 1. In some experiments, high purity (>98%) hematite powder obtained from LOBA Chemie Co. was added to the reductant mixture to investigate the effect of carbon gasification rate on the reduction rate. The temperature was measured at two different points by K-type thermocouples with a diameter of 1 mm located half through the crucible height (Figure 1).

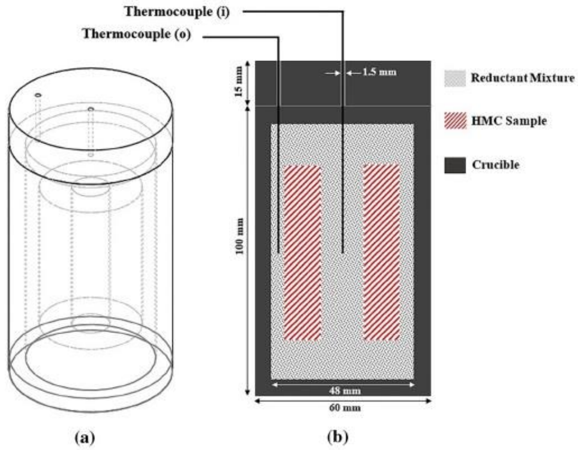

Fig. 1 Schematic of the configuration of materials and thermocouples in the crucible in (a) trimetric view and (b) front view of axial section.

The crucible was placed in the furnace at room temperature and the furnace was heated up to 1000 °C at the heating rate of 10 °C/min. In order to investigate the progress of the reduction process, the experiments were run for different durations. In all experiments, the crucible was cooled in water immediately after removal from the furnace.

TG-DTA experiments were performed by a BAHR STA 503 at a heating rate of 10 °C/min under argon atmosphere. X-ray diffractometer (XRD) analysis was conducted by a GNR device with monochromatic Cu-K_α in the angular (2θ) range of 20-90. LEO 1450 VP scanning electron microscopy was used to study the morphology of the metallic iron.

3. Results and Discussion

Time-temperature curves for T_o and T_i are drawn in Figure 2. Three distinct phenomena can be observed in these curves. Moisture evaporation is well assignable at 100°C on the T_i curve. At about 850-870°C, the endothermic decomposition of calcium carbonate can be seen as a decrease in the slope on T_i curve in Figure 2. The last endothermic reaction which can be recognized on both T_i

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and T_o curves is carbon gasification that occurs at about 930-950°C. The

decrease in the T-t curves due to the carbon gasification indicates that the rate of this reaction is limited by the heat conduction in the crucible.

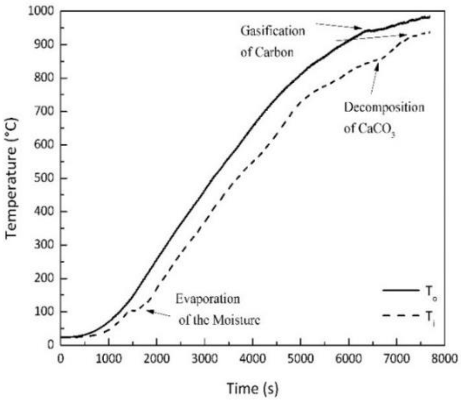

Fig. 2 Temperature-time curves obtained by the inner and the outer thermocouples at heating rate of 10 °C/min.

Figure 3 shows the results of the reduction test using graphite-calcium carbonate mixture. As can be seen, the reduction rate increases after sample T_o-900 which corresponds to carbon gasification in the outer reductant mixture. After sample T_i-950, the reduction rate decreases due to the limiting effect of gaseous diffusion of CO to the FeO-Fe interface.

In order to examine the effect of gasification reaction, hematite (6% of graphite) was added to the reductant mixture to enhance the gasification reaction. The results can be seen in Figure 4. Addition of hematite to the reductant mixture increased the reduction by about 9%. This can be related to carbon gasification and therefore it can be concluded that gasification reaction plays a meaningful effect on the reduction rate during the middle to the final stages.

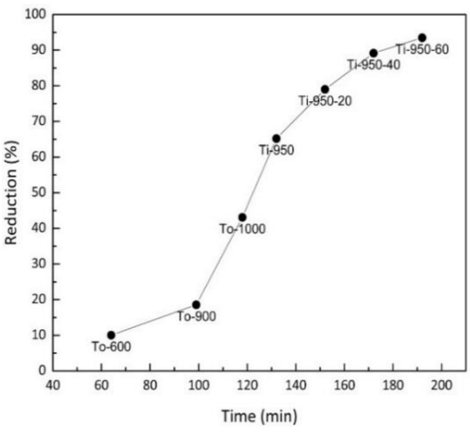

Fig. 3. Reduction progress vs time using graphite-calcium carbonate mixture as reductant.

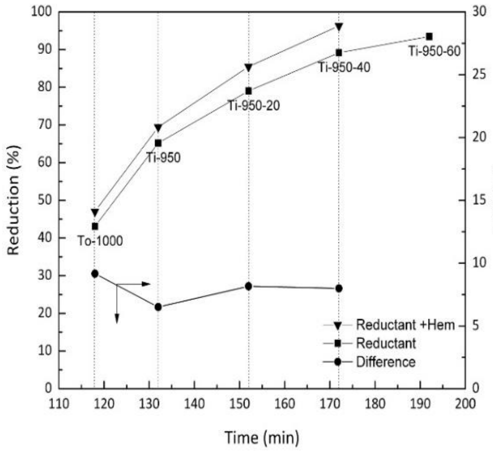

Fig. 4. Effect of hematite addition in the graphite-calcium carbonate mixture on the reduction rate versus time.

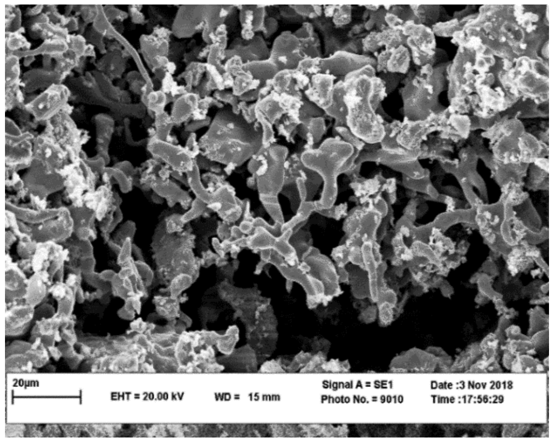

Fig. 5. Secondary electron micrograph from the metallic iron whiskers formed at the outer layer.

Fig. 5 shows the SEM images of the metallic iron layer outside the sample T_i-950-60. According to this Figure, the iron whiskers are evident in this region.

4. Conclusions

In this study, the mechanism of reduction of hematite-magnetite concentrate (HMC) with graphite-calcium carbonate reductant mixture was investigated.

- The heat transfer inside the crucible affects the initial and middle stages of the reduction process (up to 63% reduction).
- The diffusion of reducing gas to the FeO-Fe reaction interface and carbon gasification by CO_2 are the mixed controlling mechanism in the middle to the final stages of the process (63% to 93% reduction).