Kinetics and Mechanism of Carbothermic Reduction of Magnesia

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The reaction between MgO and graphite powders under flowing argon atmosphere was studied using a dynamic thermogravimetric method. In the temperature range 293 to 1973 K, the effects of compacting pressure, magnesia/carbon ratio, heating rate, Ar carrier-gas flow rate, and CO-partial pressure were investigated. An experimentally determined reaction mechanism was proposed and discussed. The reaction process could be divided into two stages. The first stage includes the direct reaction between MgO and graphite particles and partial gas-solid reaction at relatively low temperature (below 1750 K). The overall reaction rate depends on the solid phase-boundary reaction between magnesia and carbon particles. The second stage is the gas-solid reaction between CO and MgO, which determines the overall reaction rate. The apparent activation energies of the two stages were estimated to be 208.29 and 374.13 kJ/mol, respectively.

I. INTRODUCTION

MAGNESIUM is the lightest of all the commonly used structurated metals. This property entices automobile manufacturers to replace denser materials, not only steels, cast irons, and copper-based alloys, but even aluminum alloys with magnesium-based alloys. The requirement to reduce the weight of car components and further introduction of legislations to limit emissions have triggered renewed interest in magnesium.[1] Magnesium is produced by two principal processes: electrolysis of molten magnesium chloride and thermal reduction of magnesia. Electrolysis is the predominant route, accounting for about 77 pct of total production, but this process is characterized by high-energy requirements.[2] The reaction between MgO and C may provide a new route toward the production of magnesium. Furthermore, MgO/C refractory bricks are widely used in the steelmaking industry as basic oxygen furnace (BOF) linings. However, a serious problem in using BOF bricks is that the reaction between magnesia and carbon takes place when they are used under the steelmaking condition at about 1873 K for a long time, which leads to a decrease of their strength and lifetime. Pickering found that weight and strength losses were observed experimentally in the 1773 to 1873 K temperature range, and the reduction of magnesia by carbon produced extensive microstructural changes.[4] Despite the importance of the performance of the BOF magnesia bricks in the steelmaking industry, a systematic study dealing with reduction kinetics of magnesia by carbon has not been reported.

To obtain the high-quality steels and so-called "clean steel," their content of oxygen, sulfur, phosphorus, and nitrogen must be decreased to ultralow concentration. Alkaline earth metals, especially magnesium, have attracted many researchers’ interest, owing to their strong chemical affinity to these nonmetallic elements. Recently, our research group developed a new desulfurization and deoxidation method of molten iron using magnesium vapor produced in situ by carbothermic reduction of magnesia.[5,6] The kinetics of the reduction of magnesia by carbon is one key point in controlling the process of desulfurization and deoxidation and finding a more efficient way to promote the desulfurization and deoxidation efficiency and the rate. The complexity of the reduction process makes it difficult to gain a clear insight into the various steps involved in the overall reduction process. Hence, it is necessary to study and clarify the mechanism and kinetics of the carbothermic-reduction process.

In this study, emphasis is focused on the kinetics of the reaction between magnesia and graphite powder in the flowing-argon atmosphere. The effects of compacting pressure, magnesia/carbon ratio, heating rate, CO-partial pressure, and Ar flow rate is discussed. A reaction mechanism based on the nonisothermal gravimetric analysis is also proposed.

II. EXPERIMENTAL

The magnesia powder (0.4 μm in average diameter, and purity higher than 99.99 pct) and graphite powder (fixed carbon 99.12 pct, ash 0.15 pct, water 0.4 pct, and average diameter 3.9 μm) were used as starting materials. Magnesia and graphite powder were mixed with molar ratios of 1:1 and 1:2. The mixtures were compacted into 5-mm-diameter pellets under compacting pressures of 100 and 150 MPa using a cold isostatic press. The dimensions of the graphite crucible used in this study are 6.4 mm in outside diameter, 5.8 mm in inside diameter, and 5.5 mm in height.

The reduction reactions were carried out using a thermobalance (NS95, Sinki-riko, Corporation, Tokyo, Japan), which has a detection precision of 1 μg for temperature up to 1973 K. The temperature was controlled with PtRh6 pct/PtRh30 pct thermocouple, which has a detection precision of ±1 K. The system was connected to a computer data-acquisition and analysis system. The sample was put into the graphite crucible, which was positioned on the top of the thermocouple.
The inert atmosphere was maintained by allowing argon to flow at a rate of $1.67 \times 10^{-6} \text{ m}^3/\text{s}$. After the air in the furnace was purged with argon for 30 minutes, the sample was heated from room temperature to 773 K and held at this temperature for 10 minutes to remove the absorbed gases and water from the sample. Then, the temperature was raised to 1973 K at different heating rates. To correct the effect of the graphite crucible on the mass loss of the sample, blank experiments were carried out using the blank-graphite crucible. The calibration runs were, of course, carried out under the same conditions as those used for samples. The morphology of the sample before and after reduction was examined by a scanning electron microscope (SEM, S-450, Hitachi, Tokyo, Japan) in the secondary electron-image mode.

### III. RESULTS AND DISCUSSION

The following reactions may occur during the reduction process of magnesia by carbon:

**Direct reduction:**
$$\text{MgO} + \text{C} = \text{Mg} + \text{CO} \quad [1]$$

**Indirect reduction:**
$$\text{MgO} + \text{CO} = \text{Mg} + \text{CO}_2 \quad [2]$$
$$\text{CO}_2 + \text{C} = 2\text{CO} \quad [3]$$

During the thermogravimetric reduction experiment, the mass loss of the sample was monitored as a function of time. The reduction ratio ($\alpha$) at a given instance is defined as

$$\alpha = \frac{\Delta W}{W_0} \quad [4]$$

where $W_0$ represents the initial mass of magnesium in the sample, and $\Delta W$ is the magnesium-mass change at that instance.

A typical mass-loss percentage vs temperature curve of reduction of magnesia by carbon is shown in Figure 1. It is clear that there is no mass loss detected when the temperature is below 1100 K, indicating no reaction happens. When the temperature is higher than 1100 K, there are two stages of mass loss found. In stage I (temperature range 1100 to 1750 K), the reduction rate of magnesia by carbon is extremely slow. The mass loss is less than 15 pct of the total mass, and the reduction ratio is less than 0.25. In stage II (temperature above 1750 K), the sample weight changes sharply with the increase of temperature.

Figure 2 shows the SEM micrographs of the pellets of magnesia and carbon before and after experiments at different reduction ratios ($\alpha$). In SEM micrographs, the layered-structure particles are carbon, and the granular-structure particles are MgO. From the micrograph (Figure 2(a)), it can be seen that the mixing condition between magnesia and carbon particles is good before experiment. As the reduction processes and the temperature increases, it is found that the particle size of carbon increases, and high reaction temperature gives rise to the densification of magnesia, which leads to the grain growth of MgO (Figures 2(b) and (c)). All these factors result in the decrease of the contacting area between magnesia and carbon particles.