Kinetics and Mechanism of Carbothermic Reduction of Magnesia

LI RONGTI, PAN WEI, and MASAMICHI SANO

The reaction between MgO and graphite powders under flowing argon atmosphere was studied using a dynamic thermogravimetric method. In the temperature range 293 to 1773 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 reduction 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 structured 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 magnesium. 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 to the production of magnesium. Furthermore, MgO/C refractory bricks are widely used in the steelmaking industry as basic oxygen furnace (BOF) linings because of their good resistance both to slag corrosion and thermal stresses.[3] 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 are 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, Sinku-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: $\text{MgO}_{(s)} + \text{C}_{(s)} = \text{Mg}_{(g)} + \text{CO}_{(g)}$ \[1\]

Indirect reduction: $\text{MgO}_{(s)} + \text{CO}_{(g)} = \text{Mg}_{(g)} + \text{CO}_{2(g)}$ \[2\]

$\text{CO}_{2(g)} + \text{C}_{(s)} = 2\text{CO}_{(g)}$ \[3\]

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

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

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.
The effect of the compacting pressure of the samples on the reduction rate is shown in Figure 3. It is found that the rate of reduction increases significantly when the compacting pressure increases from 0 to 100 MPa. Increasing compacting pressure will help to increase the contacting area between magnesia and carbon particles, which leads to the increase of reduction rate. Figure 3 also shows that the reduction rate difference between samples formed at 100 and 150 MPa is quite small. This may be due to the fact that when the packing density of the sample is close to the maximum value, the contacting condition can no longer be improved by just increasing the sample-forming pressure.

The effect of the magnesia/carbon ratio on the reduction ratio is shown in Figure 4. It can be seen that, in the initial stage (\( \alpha < 0.25 \)), the reduction rate increases evidently when increasing carbon content. It indicates that an effective increase of the reduction rate can be achieved by increasing the carbon content in magnesia and carbon mixtures. With the increase of carbon content in the mixture, the contacting area between magnesia and carbon particles increases, which accelerates the reduction of magnesia by carbon.

The results of the nonisothermal reduction ratio at different heating rates are presented in Figure 5. As can be seen, all the reduction curves show a similar trend with a difference in just the slope of each curve. The reduction ratio at a given temperature decreases with the increase of heating rate, especially when the temperature is above 1800 K.

The effect of argon-flow rate on the reduction ratio is shown in Figure 6. It is found that the reduction rate increases with the increase of Ar carrier-gas flow rate only when the reduction ratio (\( \alpha \)) is less than 0.25. Otherwise, the reduction rate decreases with the increase of Ar carrier-gas flow rate. From Eq. [1], it can be seen that with the increase of the Ar carrier-flow rate, the concentration of magnesium vapor and CO decreases, which will accelerate the reduction process of magnesia. At the same time, Reaction [2] will slow down because of the decrease of the CO concentration. It indicates that, in the initial stage (\( \alpha < 0.25 \)), the solid phase-boundary reaction (Reaction [1]) is the main process. From Reactions [2] and [3], it can be seen that the decrease of partial pressure of CO and CO\(_2\), caused by the increase of the Ar carrier-flow rate, reduces the rates of reaction between MgO and CO and reaction between CO\(_2\) and carbon. Based on the observation that increasing the Ar-flow rate decreases the whole reduction rate (when \( \alpha > 0.25 \)), we concluded that the gas-solid reactions (Reactions [2] and [3]) are the rate-determining steps in the second stage.
The relationship between reduction rate and CO-partial pressure is \( r_{\text{PA}:/text{PCO}=9:1} > r_{\text{PA}:/text{PCO}=8:2} > r_{\text{PA}:/text{lamb}} \) (\( r \): reduction rate) (Figure 7). It indicates that slightly increasing the CO-partial pressure will lead to a significant increase of the reduction rate. From Reactions [2] and [3], it can be deduced that the former is more sensitive to the increase in CO-partial pressure than that of the latter, and it is the reaction between magnesia and CO that determines the overall reaction rate. As Reactions [2] and [3] are interconnected and interdependent, too high a CO-partial pressure reduces the reaction rate of the latter, which, in turn, will reduce the reaction rate of the former.

IV. DESCRIPTION OF THE REACTION MECHANISM

During the past decades, numerous studies have been conducted on the carbothermic-reduction mechanism of metal oxides.[7–12] Several mechanisms have been proposed to explain the interaction of two solid reactants (metal oxide and carbon) with the formation of solid metal or metal carbide, but some apparent contradictions in the experimental results have led to a number of different interpretations of the reaction mechanism.

In the system of present study, the reduction of magnesia by carbon, there are some differences from the previous investigations on the carbothermic reduction of metal oxides. Under the inert atmosphere and flow conditions, the reduction of MgO by C was carried out at above 1393 K, the boiling point of magnesium. Thus, products of the reaction between magnesia and carbon are gaseous. This rules out the possibility of mass diffusion through the product matrix as the rate-determining step.

Based on our thermal analysis results, the reaction mechanism proposed is schematically shown in Figure 8. The whole reduction process can be described as follows.

1. The CO and Mg vapor are formed at the contact points of the carbon and magnesia particles, according to reaction [1], at the beginning. This process is the solid phase-boundary reaction between the magnesia and carbon particles. The reaction rate is very sensitive to both the particle size and to the relative proportion of the solid reactants. The overall reduction rate increases with the increment of the boundary area between MgO and C particles, which can be realized by increasing the compacting pressure and the molar ratio of C/MgO.

2. As the reduction progresses, the particle size increases, and the contacting area between magnesia and carbon particles decreases. The solid phase-boundary reaction between magnesia and carbon particles is no longer the main process. The reactions proceeding through gaseous intermediates (Reactions [2] and [3], Figure 8) subsequently become the main reaction process.

In the second stage, the possible rate-determining steps are (1) the chemical reaction (Reaction [2] or [3]) and (2) the diffusion of gases through the porous media. The diffusion coefficients of magnesium vapor and CO through the porous media are 6.87 \( \times 10^{-5} \) (m\(^2\)/s) and 9.25 \( \times 10^{-5} \) (m\(^2\)/s) at 1848 K, respectively, which were calculated based on the Chapman–Enskog theory and effective diffusion-coefficient equation.[13] It indicates that at high temperatures magnesium vapor and CO diffuse quickly through the porous media, so the diffusion of gas through porous media is not likely to be the rate-determining step. The reaction of CO with carbon is rather slow at temperature below 1273 K. Numerous investigations on the reduction of metal oxides at low temperature have been conducted and concluded that the reaction of CO\(_2\) with solid carbon determines the overall reaction rate. But at high temperature, the reaction of CO\(_2\) with carbon is rather quick, so it is impossible that this reaction controls the overall reduction rate. In the magnesia and carbon reduction system, the concentration of CO\(_2\) at 1573 K is only 2.30 \( \times 10^{-5} \) Pa (calculated based on the Gibbs free energy of Reactions [1] and [3]) and even lower at higher temperature. This indicates that the conversion of CO\(_2\) to CO on the solid carbon is very fast, and the regener-ated CO supports the continuation of the reduction of magnesia. Thus, it is deduced that the reaction between MgO and CO is the rate-determining step in the second stage. The reaction rate of the reduction of magnesia by carbon can be expressed as

\[
\frac{dm}{dt} = k(T)f(\alpha) \tag{5}
\]

where \( f(\alpha) \) is a function of \( \alpha \) and \( k(T) \) is the rate constant, whose relation with temperature can be given by the Arrhenius equation as

\[
k(T) = A \exp \left(-\frac{E}{RT}\right) \tag{6}
\]
where \( A \) is the pre-exponential constant, \( R \) is the gas constant, and \( E \) is the activation energy. Substituting Eq. [6] into [5] and taking logarithms, one obtains

\[
\ln \left( \frac{da}{dt} \right) = \ln \left( k_0 f(a) \right) - \frac{E_a}{R} \frac{1}{T} \tag{7}
\]

In Eq. [7], \( f(a) \) is only determined by \( a \). When we choose the data of \( da/dt \) and the absolute temperature, \( T \), at the same value of \( a \) from the experiments of different heating rates, there should be a linear relationship between the chosen \( \ln \left( \frac{da}{dt} \right) \) and \( \frac{1}{T} \). The slope of the line gives the apparent-activation energy \( E_a \).

The apparent-activation energy of both stages was calculated. The plots of \( \ln \left( \frac{da}{dt} \right) \) vs \( \frac{1}{T} \) at various \( a \) are shown in Figure 9. An average \( E_a \) value of 208.29 kJ/mol was obtained in the range 0.1 < \( \alpha < 0.25 \) for the initial stage and 374.13 kJ/mol in the range 0.25 < \( \alpha < 0.5 \) for the second stage. By applying the transition state theory (TSP)\(^{[14]}\) we calculated values of the activation energy for reactions [2] and [3]. They turn out to be 470 and 180 kJ/mol in the temperature range 1573 to 1873 K for Reactions [2] and [3], respectively. The experimental \( E_a \) value for the second stage is quite close to the calculated \( E_a \) value for Reaction [2], indicating the Reaction [2] is the rate-determining step in the second stage.

V. CONCLUSIONS

Reduction kinetics of magnesia and carbon powders was investigated using the nonisothermal gravimetric technique in the temperature range from room temperature to 1973 K. Experiments were carried out under argon atmosphere, and the mass loss of the sample was determined as a function of time. Temperature, compacting pressure, carbon/magnesia ratio, heating rate, flow rate of Ar carrier gas, and the CO-partial pressure all significantly affect the reduction kinetics. An experimentally determined reaction mechanism was proposed and discussed. The rate-determining step of the reduction of magnesia by carbon was determined. In the initial stage of reduction, the solid phase-boundary reaction determines the reduction rate, and the average activation energy is 208.29 kJ/mol. In the second stage, the reaction between MgO and CO becomes the rate-determining step for the overall process, and the average activation energy is 374.13 kJ/mol, which is close to the calculated value (470 kJ/mol) based on TST.

REFERENCES