Carbothermic and Aluminothermic Reduction of Solid Oxide

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An investigation of the reduction of magnesia and chromia by graphite and aluminum was carried out using a nonisothermal gravimetric technique under an argon atmosphere, in a temperature range from 600 to 1973 K. In the case of MgO–C system, the reduction ratio obtained by using charcoal is larger than that by using graphite. An excess charcoal addition increases the reduction ratio. The activation energy is 192.4–208.1 kJ/mol. The Boudouard reaction has a large influence on the reaction rate. In the case of MgO–Al system, magnesia is reduced by aluminum to form magnesium and spinel at first, and then the excess aluminum reacts with the spinel slowly. The reaction rate is affected by pellet-forming conditions. The activation energy of the reduction of magnesia by aluminum is 151.2 kJ/mol. In the case of Cr₂O₃–C system, the reduction reaction proceeds through two steps. At first, chromia is reduced by graphite to form chromium carbide, and then the rest of chromia by the chromium carbide. The excess graphite addition increases the reduction ratio, but chromium carbide and not chromium is obtained.

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1. Introduction

Considerable quantities of waste bricks are generated in the iron and steel industry. There are increasing environmental problems associated with their dumping or accumulation.1) Usually, the waste bricks contain many valuable metals,2) such as magnesium, chromium, etc. In iron- and steel-making processes, magnesium3)–6) has been well known as one of the excellent refining reagents, because of its high reactivity. Since its production is energy intensive, the price is very high. Thus magnesium has not widely been used as a reagent in metal refining processes. Chromium is one of the alloying elements of stainless steels. The selective recovery of magnesium and chromium could be achieved by the carbothermic and aluminothermic reduction of the waste bricks. Aluminum has been used as the reducing agent in many oxides, which otherwise are reduced by carbon with difficulty.7)–9)

In the present study, the reduction of magnesia and chromia by graphite and aluminum was carried out using a nonisothermal gravimetric technique under an argon atmosphere, in a temperature range from 600 to 1973 K. The experiments were carried out for MgO–C, MgO–Al, Cr₂O₃–C, Cr₂O₃–MgO–C and Cr₂O₃–Fe₂O₃–C systems.

2. Experiment

2.1 Materials

The materials used in this study were powders of magnesia 0.4 μm, purity 99.99%, charcoal less than 44 μm, purity 90%, graphite 3.9 μm, purity 99.12% and 19.2 μm, purity 99.43%, aluminum 75–150 μm, purity 99.5%, spinel (MgO·Al₂O₃), 91.2% of which is less than 18.74 μm, purity 99.9%, chromium oxide less than 44 μm, purity 99.98%, and hematite 0.6–0.7 μm, purity 98%. For the carbothermic reduction experiment, homogeneous mixtures with magnesia: carbon molar ratios of 1:1 and 1:2, and with chromia: carbon molar ratios of 1:3 and 1:6 were prepared. In some experiments of carbothermic reduction of chromia, magnesium or hematite was added to the mixture. The initial weight of the powder sample was about 20–60 mg. For the aluminothermic reduction experiment, a homogeneous mixture with a molar ratio of magnesia: aluminum as 3:2 was prepared, and in some experiments, lime of 24.3 mass% was added to the mixture. The mixture was formed into a 5 mm diameter pellet under sample forming pressures of 10, 50 and 150 MPa using a cold isostatic press. The sample was dried in a vacuum desiccator. The initial weight of the sample was about 40 mg.

2.2 Apparatus and experimental procedure

The experiments were carried out with a thermobalance, which has a detection precision of 1 μg, for temperatures up to 2050 K. The apparatus is schematically shown in Fig. 1. The system was fully controlled by a personal computer (PC). The crucible was made of graphite and its size was 6.4 mmφ × 5.8 mmφ × 5.5 mmH. The sample was put into the graphite crucible, the bottom of which touched with a thermocouple. In the case of magnesia reduction experiment, the atmosphere was argon or CO with a flow rate of 2.5 × 10⁻⁶ Nm³/s. After waiting for 1200 s for the air in the furnace to be substituted with Ar or CO, the sample was heated from room temperature to 773 K and maintained at this temperature for 600 s to remove all adsorbed gases and water. The temperature was then raised to 1273 K, at a heating rate of 3.33 K/s. From 1273 K to 2050 K, the sample was heated at a constant heating rate (0.33 ~ 1.67 K/s). In the case of chromia reduction experiment, the atmosphere was argon with a flow rate of 2.33 × 10⁻⁶ Nm³/s. After waiting for 1200 s for the air in the furnace to be substituted with Ar, the sample was heated from room temperature to 523 K and maintained at this temperature for 120 s to remove all adsorbed gases and water. The temperature was then raised at a constant heating rate (0.33 ~ 1.67 K/s). The weight change was measured at 1 s intervals and was input into the PC. Repetition of several experiments showed fair

![Fig. 1. Schematic diagram of thermobalance device.](image-url)
reproducibility.

3. Theory

Kinetics of solid state reaction is influenced by many variables, such as sample composition, particle size and its distribution, reaction products, sample forming pressure and heating rate, etc.

For the irreversible reaction,

\[ mA(s) + nB(s or l) \rightarrow pC(s) + qD(g) \quad (1) \]

the reaction rate may be expressed as

\[ \frac{d\alpha}{dt} = k(T)A(\alpha)\alpha a^n \quad (2) \]

where \( A(\alpha) \), a function of reduction ratio \( \alpha \), is the reaction interface area (m²), \( a_A \) and \( a_B \) are the activities of reactants A and B, respectively (for pure A and B, \( a_A = a_B = 1 \)), \( k(T) \) is the rate constant (\text{min}^{-1}\cdot\text{m}^{-2}) whose relation with temperature can be given by Arrhenius equation as

\[ k(T) = f \exp(-E/RT) \quad (3) \]

where \( f \) is the pre-exponential constant (\text{min}^{-1}\cdot\text{m}^{-2}) \( R \) is the gas constant (kJ/mol-K) and \( E \) is the activation energy (kJ/mol). Here, it is assumed that \( A(\alpha) \) is dependent only on the reduction ratio.

4. Results and Discussion

4.1 MgO-C system

The overall reaction of carbothemic reduction of magnesia is expressed as

\[ \text{MgO(s) + C(s) = Mg(g) + CO(g)} \quad (4) \]

The elementary reactions are

\[ \text{MgO(s) + CO(g) = Mg(g) + CO}_2(g) \quad (5) \]

\[ \Delta G = 451.21 - 0.12147 \text{kJ/mol} \]

\[ \text{CO}_2(g) + C(s) = 2\text{CO(g)} \quad (6) \]

\[ \Delta G = 161.54 - 0.167927 \text{kJ/mol} \]

Equation (6) is called as the Boudouard reaction.

The reduction ratio, \( \alpha \), is defined as the ratio of magnesium weight loss, \( \Delta W \), caused by the reduction to the initial magnesium weight in the sample, \( W_0 \).

\[ \alpha = \Delta W/W_0 \quad (7) \]

**Figure 2** shows the relation between reduction ratio and temperature. In the figure, comparison of magnesia reduction ratios for charcoal and graphite is investigated. As shown in the figure, the reduction ratio for charcoal is larger than for graphite. **Figure 3** shows the influence of a molar ratio of magnesia : carbon on the reduction ratio. The reduction ratio increases large by adding excess charcoal. **Figure 4** shows the effect of atmospheric gas on the reduction ratio. The reduction ratio under CO atmosphere is smaller than that under Ar atmosphere. **Figure 5** shows the effect of the sample heating rate on the reduction ratio. With increasing heating rate, the reduction time decreases and hence the reduction ratio becomes smaller.

The reduction rates at the reduction ratios of 0.2, 0.3, 0.4 are obtained from Fig. 5. **Figure 6** shows the relation between reduction rate and temperature. The apparent activation energy obtained is from 192.4 to 208.1 kJ/mol and independent of the reduction rate. This value is close to the value of the activation energy of the Boudouard reaction.11)

4.2 MgO-Al system

**Figure 7** shows a typical weight loss-temperature curve of the magnesia-aluminum reaction. From the figure, it is clear
that there are two stages of weight change with temperature. Until the temperature reaches at 1450 K, the reaction does not occur or is extremely slow. The weight loss in the beginning of the experiment is due to the removal of adsorbed gases in the sample and crucible. This has been proved by the results of blank experiment. In the following analysis, the weight loss caused by the adsorbed gases is eliminated. The threshold temperature for the kinetic analysis is taken as 1300 K. In the first stage of reduction curve, the sample weight changes with temperature sharply. Then in the second stage, again, the weight change becomes slow. The critical temperatures $T_1$ and $T_2$ represent the temperatures, at which the first and the second stages start. It is found that the reaction between magnesia and graphite crucible can be ignored at the present temperature, because its rate is slower and the contact area is very small between magnesia and crucible.

The following reactions may occur during the reduction of magnesia by aluminum.

$$4\text{MgO}(s) + 2\text{Al}(l) = 3\text{Mg}(g) + \text{MgO} \cdot \text{Al}_2\text{O}_3(s) \quad (8)^{12}$$

$$\Delta G^0 = 465.6 - 0.287T \text{kJ/mol}$$

$$3(\text{MgO} \cdot \text{Al}_2\text{O}_3(s) + 2\text{Al}(l) = 3\text{Mg}(g) + 4\text{Al}_2\text{O}_3(s) \quad (9)^{12}$$

$$\Delta G^0 = 607.7 - 0.279T \text{kJ/mol}$$

The sample after stage I was analyzed by X-ray diffraction. It showed that the sample is mainly a mixture of spinel and aluminum. An experiment on reduction of pure spinel by aluminum was carried out. The result is shown in Fig. 8. The reduction ratio changes very slowly with temperature. This is quite similar to the reaction occurring in stage II. The maximum reduction ratio is 75% at which magnesia changes to spinel thoroughly according to Reaction (8). The actual reduction ratio at the end of stage I is 70 ÷ 75%.

Figure 9 shows the relation between reduction ratio and temperature for various heating rates. The critical temperatures $T_1$ and $T_2$ increases with increasing heating rate, $\beta$. Figure 10 indicates the relation between reduction ratio and temperature for various sample forming pressures. The critical temperatures $T_1$ and $T_2$ decreases with increasing sample forming pressure.

At the present experimental temperatures, liquid aluminum drops are dispersed in solid magnesia powders. Hence, the aluminothermic reduction of magnesia is similar with its carbothermic reduction, and should be treated as a solid state reaction. Hence, Equations (1) à (3) are also applied to the MgO-Al system.

For a linear heating rate,

$$T = T_0 + \beta t \quad (10)$$

$$dT/dt = \beta \quad (11)$$

where $T_0$ is the initial temperature (K), $\beta$ is the linear heating rate (K/min).

The basic kinetic equation describing non-isothermal kinetic data is obtained by combining the above equations.
In the present study, the reduction ratio changes almost linearly with temperature in stage I, as shown in Fig. 9. The difference in $\frac{da}{dT}$ with the heating rate is not large. The average value of $\frac{da}{dT}$ is calculated as $(4.92 \pm 0.62) \times 10^{-3}$ K$^{-1}$ in the reduction ratio range from 0.15 to 0.70. Since $f(A)$ should be constant for a given reduction ratio, the left-hand side of Eq. (12) is constant, which does not depend on the heating rate and the temperature. Then, one can obtain

$$\ln \beta + E/RT = \text{const.} \quad (13)$$

Thus, the plot of $\ln \beta$ versus reciprocal absolute temperature for a given value of reduction ratio, $\alpha$, gives a straight line, from the slope of which one can obtain the activation energy.

The relation between $\ln \beta$ an $1/T$ is shown in Fig. 11 for three reduction ratio values of 0.10, 0.31 and 0.52. The value of activation energy is $146.2 \sim 154.5$ kJ/mol.

The weight loss is caused by the evaporation of magnesium, which is proportional to the vapor pressure of produced magnesium. Therefore, the theoretical activation energy may be calculated from the relation between the magnesium vapor pressure and temperature assuming that the reaction reaches its equilibrium state. For Reaction (8), $\ln (P_{Mg}) = -18685/T + 11.52$, $E = 155.3$ kJ/mol, where $P_{Mg}$ is the equilibrium magnesium vapor pressure (atm). This value is close to the experimental result and confirms that Reaction (8) proceeds in stage I.

The effect of the mass-transfer process on the reaction was also investigated. For the same temperature and reaction time, the reduction ratio of magnesia by aluminum under the condition of an argon atmosphere (pressure of 0.101 MPa, and flow rate of $1.67 \times 10^{-6}$ Nm$^3$/s) is almost the same as under the condition of vacuum (argon pressure of 334 kPa). This implies that the mass-transfer process does not contribute to the controlling step.

The effect of lime addition on the reaction rate is shown in Fig. 12. It is seen that lime addition accelerates the reaction. The reaction product may be partly melted for the sample with lime addition. This is because the compound of lime and alumina has a lower melting point than spinel. This improves the contacting condition between magnesia and aluminum. For the sample with lime addition, no apparent spinel reduction stage is observed.

The reduction of spinel by aluminum is very slow. In order to improve the reduction rate of magnesia, it is necessary to inhibit the formation of spinel. Lime addition is proved to be effective for this purpose.

### 4.3 Cr$_2$O$_3$–C system

The reduction ratio, $\alpha$, is defined as the ratio of oxygen, carbon and magnesium weight loss, $\Delta W$, caused by the reduction to the initial oxygen, carbon and magnesium weight in the sample, $W_0$.

$$\alpha = \Delta W/W_0 \quad (1')$$

Figure 13 shows the comparison of reduction ratios for different molar ratios of chromia to graphite. In the case of the ratio of 1 : 3, it is clear that there are two stages of reduction ratio change with temperature. In the first stage, the reduction ratio increases with increasing temperature rapidly, while slowly in the second stage. The reaction between chromia and graphite crucible can be ignored at the present experiment, because the contact area is very small between chromium oxide and crucible.

The sample after stage I was analyzed by X-ray diffraction. It is found that the sample is mainly a mixture of Cr$_2$O$_3$ and Cr$_7$C$_3$. The following reactions may occur during the reduction of chromia by carbon.

$$7\text{Cr}_2\text{O}_3(s) + 27\text{C}(s) = 2\text{Cr}_7\text{C}_3(s) + 21\text{CO}(g) \quad (14)$$

$$\text{Cr}_2\text{O}_3(s) + \text{Cr}_7\text{C}_3(s) = 9\text{Cr}(l) + 3\text{CO}(g) \quad (15)$$

By adding excess graphite, the reduction ratio becomes large and there is only one stage of reduction ratio, as shown in Fig. 13. The sample after the experiment with excess graphite addition was mainly a mixture of chromium and chromium carbide.

Figure 14 shows the effect of the sample heating rate on the
reaction was increased because MgCr$_2$O$_4$ was much stable. On the other hand, the hematite addition accelerates the reaction. In the early stage of the reduction reaction, hematite was reduced at first. Then chromia was reduced consecutively. The iron produced by the reduction may be melted and the contacting condition between chromia and carbon was improved.

5. Conclusions

The kinetics of reduction of magnesia and chromia by carbon and aluminium were investigated with using non-isothermal gravimetric technique. The following results are summarized.

For MgO–C system,

1. The reduction ratio obtained by using charcoal is larger than that by using graphite.

2. Excess charcoal addition to the MgO–C mixture increases the reduction ratio.

3. The reduction ratio under CO atmosphere is smaller than that under Ar atmosphere.

4. The apparent activation energy of 192.4~208.1 kJ/mol is obtained under the present experimental conditions.

5. The Boudouard reaction (CO$_2$(g) + C(s) = 2CO(g)) has a large influence on the reaction rate.

For MgO–Al system,

6. The reaction takes place in two stages. Magnesia is reduced by aluminum to form magnesium vapor and spinel (MgO·Al$_2$O$_3$), and then the reduction of the spinel by aluminum occurs to release magnesium vapor slowly.

7. The activation energy of the reaction in stage I is evaluated as 146.2~154.5 kJ/mol from the experimental results for various heating rates.

8. The reduction of magnesia by aluminum is largely affected by the sample forming pressure. Higher sample forming pressure favors the reaction. This is due to the improvement of powder contacting condition.

9. Lime addition favors the reaction. This is because the compound of alumina and lime has a lower melting point than that of spinel.

For Cr$_2$O$_3$–C system,

10. The reaction takes place in two stages. Chromia is reduced by graphite to form chromium carbide, and then the reduction of chromia by the carbide occurs.

11. Excess graphite addition to the Cr$_2$O$_3$–C mixture increases the reduction ratio and forms chromium carbide.

12. The apparent activation energy of the reaction is evaluated from 270.1 to 292.8 kJ/mol in stage I and from 326.9 to 359.2 kJ/mol in stage II from the experimental results for various heating rates.

13. Magnesia addition delayed the reduction reaction, while hematite addition accelerates the reaction.
References


