Mechanism of Carbothermic Reduction of Chromium Oxide

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The isothermal experiment of carbothermic reduction of chromium oxide was carried out. The reduction rate increased by increasing temperature, using a moderate carrier gas flow rate and the fine graphite particles.

XRD analysis revealed that Cr$_3$C$_2$, Cr$_7$C$_3$, Cr$_{23}$C$_6$ and Cr were formed in turn as the reaction products at 1673 K. The relation among the products, reduction temperature and time was summarized from the XRD results at the temperature range from 1373 to 1673 K. It is confirmed that the reduction contains various kinds of reactions, such as direct reduction, indirect reduction of chromium oxide, the carbon solution loss reaction and the reaction of chromium carbide with carbon dioxide. At the initial stage of reduction, the direct reduction dominates the reduction rate. At the later stage of reduction, because of the chromium carbide layer formed on the surface of graphite particles and rather slow reduction rate, the rate-controlling step is deduced to be CO and CO$_2$ gas diffusion through the layer of reduction products.

KEY WORDS: carbothermic reduction; chromium oxide; isothermal reduction; pellet; chromium carbide.

1. Introduction

It is well known that carbothermic reduction of chromium ore is one of the possible methods for producing ferrochromium. Chromium oxide is often used as the refractory material such as the inner wall in secondary refining furnaces. For example, chrome–magnesite brick is widely used in the refining furnace for producing stainless steel. This kind of chrome–magnesite brick contains Cr$_2$O$_3$ by 13.0%. However, when chromium oxide reacts with CaO or alkali oxide at a high temperature, hexavalent chromium is liable to generate, which is very harmful to human health. If the wasted chrome–magnesite refractory bricks are reclaimed in the earth, hexavalent chromium tends to liquate out. This gives rise to serious soil pollution. One of detoxifying treatment of hexavalent chromium is carbothermic reduction of chrome–magnesite brick with addition of iron to produce ferrochromium and magnesium oxide.

Carbothermic reduction of chromium oxide under vacuum was reported by Kitada et al. The reaction of Cr$_2$O$_3$ under vacuum proceeds as follows: (1) formation of chromium carbides by interfacial reaction between chromium oxide and carbon below 1373 K. (2) formation of chromium metal by interfacial reaction between chromium oxide and chromium carbide at 1473–1573 K. (3) evaporation of chromium metal above 1573 K. Moreover, reaction of Cr$_2$O$_3$ with Cr$_7$C$_3$ or Cr$_{23}$C$_6$ was also possible to proceed.

Katayama et al. conducted carbothermic reduction of chromium oxide in the presence of argon gas at the temperature of 1263–1443 K, and divided reaction into three periods of incubation, acceleration and retardation. They pointed out that the nucleation of reduction products was the rate-controlling step at the incubation period, Boudouard reaction was the rate-controlling step at the acceleration period, and the reaction was controlled by the counter-current diffusion of CO and CO$_2$ through a relatively compact layer of chromium carbide at the retardation period. However, these reduction mechanisms were proposed without substantial experimental support. Especially, the formation of the layer of chromium carbide on the surface of a graphite particle needs to be supported from microscopic observation. The detailed mechanisms of the reduction and the rate processes were still unclear.

Shimoo et al. also studied the carbothermic reduction under an argon atmosphere at the temperature higher than 1743 K and studied the behaviors of smelting reduction. They indicated that the solid-phase diffusion through the product layer is rate-controlling when the chromium oxide particle size is smaller than the graphite particle size, and that the diffusion in gas pocket of chromium oxide particle is the rate-controlling step when the graphite particle size is smaller than the chromium oxide particle size. Berger et al. indicated that the carbothermic reduction of Cr$_2$O$_3$ consists of two subprocesses; the CO/CO$_2$ transport reaction and the reaction of primarily formed Cr$_7$C$_3$ with Cr$_7$O$_3$. They also investigated the effect of amount of carbon and different types of carbon on reduction rate.

Carbothermic reduction of chromium oxide was performed by the nonisothermal method using a thermobalance in our previous work, and it was concluded that the carbothermic reduction of Cr$_2$O$_3$ proceeds in two stages; the formation of Cr$_7$C$_3$ and the subsequent reduction of...
Cr₂O₃ by Cr₇C₃. The main purpose of the previous study was to investigate the carbothermic reduction rate of Cr₂O₃, Fe₂O₃ and mixture of Cr₂O₃ and Fe₂O₃ under various experimental conditions. Although the mechanism of carbothermic reduction of Cr₂O₃ was revealed to be different from that obtained by Berger et al., it was not deeply discussed.

The carbothermic reduction of Cr₂O₃ was studied by a number of researchers, and carbothermic reduction of Cr₂O₃ with carbide formation was clarified by some researchers. However, the mechanism of carbothermic reduction is very complex because of formation of three kinds of carbides, and changes of the reduction reaction with reduction progress. The ambiguity and discrepancy are found especially in the rate controlling steps of carbothermic reduction in Cr₂O₃ in the previous papers. The detailed mechanism needs to be further clarified with substantial high temperature experimental studies, such as microscopic observations and concrete component analyses of the reduction products.

In the present study, the isothermal experiments of carbothermic reduction of Cr₂O₃ are carried out at elevated temperatures. With the isothermal method, the phenomenon can be conveniently discussed regardless of the temperature increase rate. The main purpose of this work is to clarify the mechanism of carbothermic reduction of Cr₂O₃. Especially, the porous layers of chromium carbide formed on the surface of graphite particles are examined by microscopic observations and concrete component analyses of the reduction products. Since the diffusion process through the porous layers is considered to have significant influence on the reduction rate, and since the effective diffusion coefficient is affected by temperature, carrier gas flow rate and the particle size dependent porosity dependent on the particle size, the effects of temperature, carrier gas flow rate and graphite particle size on the reduction rate are investigated for a comprehensive understanding towards reduction mechanism.

2. Experimental Apparatus and Procedure

Figure 1 schematically shows the experimental apparatus. A high frequency induction furnace (15 kW, 100 kHz) was used to heat a graphite crucible of 40 mm I.D. and 100 mm in height, in which a high temperature isothermal zone was established. The inert atmosphere was maintained by blowing argon gas at a flow rate of 1.3 Nm³/s into the crucible. The graphite tube of 11 mm I.D., 15 mm O.D. and 60 mm in length had 5 holes of 1.0 mm in diameter at its lower part, through which the produced gas (carbon monoxide or carbon dioxide) together with the argon carrier gas flew out. The temperature in the tube and the crucible were measured with W·5%Re–W·26%Re thermocouples.

The pellets charged into the tube were composed of chromium oxide powders (4.8 μm in the mean diameter and 99.98% in purity) and graphite powders (One kind of graphite powders had the mean diameter of 20.3 μm and purity higher than 99.8%). The other had the mean diameter of 29.2 and the purity higher than 99.9%). Although the change in the ratio of chromium oxide and graphite powders may result in some variation of reduction products, in order to lucidly study the mechanism of carbothermic reduction of Cr₂O₃, the molar ratio is selected to be 1:3, which is stoichiometric ratio according to Eq. (1) defined later. The pellets were formed by use of a cold isostatic press under a pressure of 150 MPa for 3 600 s. The pellet mass was 0.50 ± 0.01 g before reduction, and the changes in pellet mass after reduction were measured by using an electronic balance with a detection precision of 0.1 mg.

After the temperature in the graphite crucible reached to the prescribed temperature and was stably kept constant, the graphite tube charged with pellets was promptly inserted into the high temperature zone in the graphite crucible to start the reaction. After the prescribed elapse time, the graphite tube was rapidly lifted up to a higher position in the furnace where the temperature was low, to immediately stop the reaction. By this method, the temperature inside the tube was changed rapidly with descent and ascent of the insertion tube.

The reduction degree of chromium oxide (R) is defined as:

\[ R = \frac{W_f - W_i}{W_f} \times 100\% \]

where \( W_f \) is the final mass and \( W_i \) is the initial mass of the pellets.

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The reduction degree of chromium oxide (R) is defined as:

\[ R = \frac{W_f - W_i}{W_f} \times 100\% \]
as the ratio of mass loss of the pellets during the reduction to the overall carbon monoxide mass theoretically produced during the reduction.

\[
\text{Cr}_2\text{O}_3 (s) + 3\text{C} (s) = \text{Cr} (s) + 3\text{CO} (g) \quad \text{(1)}
\]

\[
R = \frac{(W_0 - W_f) \times 3M_{\text{CO}} / (M_{\text{Cr}_2\text{O}_3} + 3M_\text{C})}{} \times 100 \quad \text{(2)}
\]

where \( W_0 \) and \( W_f \) are the initial and final pellet masses, \( M_{\text{CO}}, M_{\text{Cr}_2\text{O}_3}, \) and \( M_\text{C} \) are the molecular masses of CO, \( \text{Cr}_2\text{O}_3 \) and C, respectively.

The products of carbothermic reduction of \( \text{Cr}_2\text{O}_3 \) are identified by X-ray diffraction (XRD: CuKα radiation) at various experimental stages for the different temperatures. The microscopic morphology and composition distribution in the products are observed and analyzed by use of scanning electron microscope coupled with an energy dispersive spectrometer (SEM-EDS).

### 3. Results and Discussion

#### 3.1. Effect of Temperature on Carbothermic Reduction of \( \text{Cr}_2\text{O}_3 \)

Figure 3 shows the changes in reduction degree of chromium oxide with time at different temperatures. The argon carrier gas flow rate was \( 5.0 \times 10^{-7} \text{Nm}^3/\text{s} \). At 1673 K, the reduction degree of chromium oxide increased rapidly at first and reached 71% at 300 s. Subsequently the reduction degree increased slowly and reached 91% at 3600 s. With decreasing temperature to 1473 K and 1423 K, the reduction rate decreased significantly. The ultimate reduction degrees were 73% and 39% at 3600 s, respectively. When temperature was decreased to 1373 K, no appreciable reduction proceeded. These results show that the effect of temperature on reduction rate of chromium oxide is especially significant.

At the low temperature or at the initial stage of reduction, the reduction proceeds quite slowly. Since this experiment was carried out under inert atmosphere, the initial reaction should proceed in direct reduction reaction. The reaction rate is quite slow due to the limited contact interface area between chromium oxide and graphite particles.

Figure 4 shows XRD patterns of pellets at 1673 K. The reduction experiment was carried out at a carrier gas flow rate of \( 5.0 \times 10^{-7} \text{Nm}^3/\text{s} \). Figure 5 shows the time dependency in the XRD intensities of the strongest peaks for the identified phases using the reflections of (002) for C, (104) for \( \text{Cr}_2\text{O}_3 \), (121) for \( \text{Cr}_3\text{C}_2 \), (151) for \( \text{Cr}_7\text{C}_3 \), (511) for \( \text{Cr}_2\text{3C}_6 \) and (110) for Cr.

It is clear that the peak intensities of graphite and chromium oxide decreased as the reduction proceeded. Es-
especially the peak intensity of graphite decreased rapidly, and the diffraction peak almost disappeared after 600 s. In the meantime, the XRD peak of Cr$_3$C$_2$ increased a little at first, reached the maximal value at 120 s, and disappeared at 300 s. The intensity of the peak of Cr$_7$C$_3$ increased from 600 s, reached its maximal value at 1 800 s, and then decreased gradually. The peaks of Cr appeared only at 3 600 s.

From these results, it is considered that carbothermic reduction of chromium oxide proceeds according to following reactions. At first, direct reduction by solid carbon proceeds and carbon monoxide is produced.

\[
3\text{Cr}_2\text{O}_3 + 13\text{C} = 2\text{Cr}_3\text{C}_2 + 9\text{CO} \quad \text{(3)}
\]

\[
7\text{Cr}_2\text{O}_3 + 27\text{C} = 2\text{Cr}_7\text{C}_3 + 21\text{CO} \quad \text{(4)}
\]

Then the produced carbon monoxide reacts with chromium oxide to produce carbon dioxide.

\[
3\text{Cr}_2\text{O}_3 + 17\text{CO} = 2\text{Cr}_3\text{C}_2 + 13\text{CO}_2 \quad \text{(5)}
\]

\[
7\text{Cr}_2\text{O}_3 + 33\text{CO} = 2\text{Cr}_7\text{C}_3 + 27\text{CO}_2 \quad \text{(6)}
\]

\[
23\text{Cr}_2\text{O}_3 + 93\text{CO} = 2\text{Cr}_23\text{C}_6 + 81\text{CO}_2 \quad \text{(7)}
\]

\[
\text{Cr}_2\text{O}_3 + 3\text{CO} = 2\text{Cr} + 3\text{CO}_2 \quad \text{(8)}
\]

Additionally, the produced carbon dioxide reacts with carbon or carbide to produce carbon monoxide. Again the indirect reduction is accelerated as follows:

\[
\text{CO}_2 + \text{C} = 2\text{CO} \quad \text{(Boudouard reaction/solution loss reaction)}
\]

\[
7\text{Cr}_7\text{C}_3 + 5\text{CO}_2 = 3\text{Cr}_2\text{C}_2 + 10\text{CO} \quad \text{(10)}
\]

\[
23\text{Cr}_2\text{C}_2 + 27\text{CO} = 7\text{Cr}_23\text{C}_6 + 54\text{CO} \quad \text{(11)}
\]

\[
\text{Cr}_23\text{C}_6 + 6\text{CO}_2 = 23\text{Cr} + 12\text{CO} \quad \text{(12)}
\]

Furthermore, from results of XRD analysis, the reduction of chromium oxide by chromium carbide should proceed as follows:

\[
5\text{Cr}_2\text{O}_3 + 27\text{Cr}_3\text{C}_2 = 13\text{Cr}_7\text{C}_3 + 15\text{CO} \quad \text{(13)}
\]

\[
\text{Cr}_2\text{O}_3 + 3\text{Cr}_7\text{C}_3 = \text{Cr}_23\text{C}_6 + 3\text{CO} \quad \text{(14)}
\]

\[
2\text{Cr}_2\text{O}_3 + \text{Cr}_23\text{C}_6 = 27\text{Cr} + 6\text{CO} \quad \text{(15)}
\]

The theoretical value of reduction degree, which is calculated from Eq. (2), is 69% after finishing Reaction (3), being 78, 85 and 100% after finishing Reactions (13), (14) and (15), respectively. Actually, from the experimental data as shown in Fig. 5, reduction degree was 78% when reduction product was almost Cr$_7$C$_3$ at 300 s and being 84% when reduction product was mainly Cr$_7$C$_3$. These are well consistent with the theoretical values. As for Cr$_3$C$_2$, because Cr$_7$C$_3$ was produced nearly at the same time as that of Cr$_7$C$_3$, it is considered that Reactions (3) and (13) proceeded in parallel. Because the XRD peak of graphite disappeared at early stage of reduction at 1 673 K, the reductant agent should be the chromium carbides or the CO gas generated from Reactions (10) to (12) at the later stage of reduction.

Figures 6 and 7 show the changes in the intensities of XRD peaks of C(002), Cr$_2$O$_3$(104), Cr$_3$C$_2$(121), Cr$_7$C$_3$(151) with time at 1 473 K and 1 423 K. Since the temperatures...
were relatively low, both of Cr$_2$C$_6$ and Cr could not be produced until 3 600 s.

From results of XRD analyses, the reduction products were identified at different reduction stages for various temperatures. The relationship among reduction product, reduction temperature and time can be obtained as shown in Fig. 8. Under the present experimental conditions, it gives the reduction products formed at every reduction stage for different temperatures, clearly indicating that the reduction product appears as Cr$_3$C$_2$, Cr$_7$C$_3$, Cr$_{23}$C$_6$, Cr in turn during elapse of reduction time at a constant temperature, or for increase in temperature at a constant reduction time. The reduction products stem not only from the temperature, but also from the reduction time.

3.2. Effect of Carrier Gas Flow Rate on Carbothermic Reduction of Cr$_2$O$_3$

Figure 9 shows the effect of the carrier gas flow rate on the reduction rate of chromium oxide. At the carrier gas flow rate of 5.0 × 10$^{-7}$ Nm$^3$/s, the reduction rate was the fastest. With the carrier gas flow rate decreasing to 0 Nm$^3$/s or increasing to 3.3 × 10$^{-6}$ Nm$^3$/s, the reduction rate was decreased.

When the carrier gas flow rate is 0 Nm$^3$/s, the carbon monoxide partial pressure is high, and the direct carbothermic reduction of chromium oxide is hindered. When the carrier gas flow rate is as large as 3.3 × 10$^{-6}$ Nm$^3$/s, the carbon monoxide partial pressure is greatly decreased. This is unfavorable to the indirect carbothermic reduction of chromium oxide. Therefore, there is an optimal carrier gas flow rate, at which the highest rate of carbothermic reduction of chromium oxide can be attained.

3.3. Effect of Particle Size of Graphite on Carbothermic Reduction of Cr$_2$O$_3$

Figure 10 shows the effect of the particle size of graphite on the reduction rate of chromium oxide. The experiments were carried out under the conditions at a temperature of 1 473 K, a carrier gas flow rate of 5.0 × 10$^{-7}$ Nm$^3$/s, a mean diameter of chromium oxide of 4.8 μm and the mean diameters of graphite of 20.3 μm or 29.2 μm.

The reduction rate using smaller graphite particles was faster than that using larger graphite particles. This is because the specific surface area for the mean particle diameter of 20.3 μm is almost 1.5 times larger than that of the mean particle diameter of 29.2 μm. Therefore, the direct carbothermic reduction of chromium oxide is promoted, and the gasification reaction of graphite particles is also enhanced, which will facilitate the indirect carbothermic reaction of chromium oxide.

3.4. Microscopic Observation and Analysis of Pellets

Figure 11 shows microscopic observation of the whole pellets at different reduction stages. The green particles are chromium oxide. The white spots found often at the later stages of experiment are the produced chromium carbides and chromium metal. With progress of reduction reaction, the green chromium oxide decreased as well as the white area of the produced chromium carbides and chromium metal increased, although there was no obvious change in the pellet size.

Figure 12 illustrates microscopic observation and analysis of pellets after reduction for 1 800 s at 1 473 K. In the pictures, chromium oxide appears as fine particles and graphite is large particles.

From the line analysis across a graphite particle as shown in the composite diagram, high Cr content was detected around the periphery of a graphite particle, indicating that the reduction product layer was found around the graphite particle with progress of reduction reaction. Since the graphite particle is separated from the chromium oxide particles by the layer of the reduction product such as Cr$_7$C$_3$, the possible rate controlling steps should be: a) diffusion of CO and CO$_2$ through the layer of chromium carbide formed...
on the surface of graphite particles; b) carbon solution loss reactions by Reactions (9)–(12); c) solid diffusion of C or Cr thorough the layer of chromium carbide. Since no distinct difference in Cr concentration in the layer of chromium carbide is observed in Fig. 12, the reduction by the chromium carbide with solid diffusion of C and Cr through the layer of chromium carbide is unlikely to domin-ant the present reduction. Therefore, the remaining the rate-controlling steps are deduced to be a) and b).

**Figure 13** shows the SEM image of the pellet interior section after reduction. At the carrier gas flow rate of $5.0 \times 10^{-7}$ Nm$^3$/s, the reduction product layer became thicker on the surface of the graphite particle with increasing temperature or reduction time. The time that the layer of the reduction product completely covered the graphite particle was 120, 600 and 1 200 s at 1 673, 1 473 and 1423 K, respectively. With respect to the change in reduction degree as shown in Fig. 2, it is known that the reduction rate became rather slow after the graphite particle was covered by the reduction product layer.

As stated above, the rate-controlling step should be the carbon solution loss reactions, or the CO and CO$_2$ gas diffusion through the layer of chromium carbide formed on the surface of graphite particles. Since the carbon solution reaction is greatly accelerated at the elevated temperature, it is further deduced that the rate-controlling step is CO and CO$_2$ gas diffusion through the layer of reduction product at later stage of reduction due to the very slow reaction rate.

Although many researches have been done on the mechanism of the carbothermic reduction of Cr$_2$O$_3$, the widely accepted mechanism seems not to exist due to its complex-ity. In the present study, with the support of the substantial XRD and SEM-EDS observations and analyses together with the high temperature experimental results, the obtained mechanism of carbothermic reduction of Cr$_2$O$_3$ is in agreement with that proposed by Katayama *et al.*\(^7\) in the later stage of reduction. But it is different from that ob-tained by Shimoo *et al.*\(^8,9\) who believed that the solid-phase diffusion through the layer of product is the rate-controlling step when chromium oxide particle size is smaller than graphite particle size just as in our case.

After graphite particles were covered with the layer of the reduction product of chromium carbide, since the carbothermic reduction of Cr$_2$O$_3$ proceeded by reacting with CO gas, the produced CO$_2$ might reversely react with C or chromium carbide according to Reactions (9)–(12). Thus the overall reaction should be characterized by the apparent direct reduction of Reactions (1) and (13)–(15).
4. Conclusions

The emphasis of the present study was placed on clarification of the mechanism of carbothermic reduction of chromium oxide. Isothermal reduction experiments were carried out to investigate effects of temperature, carrier gas flow rate and graphite particle size on the carbothermic reduction rate of chromium oxide. SEM observations, EDS analyses and XRD analyses of the pellets were carried out. The conclusions can be summarized as follows:

1. The temperature has a significant effect on the reduction rate of chromium oxide. Reduction reaction is accelerated at a moderate carrier gas flow rate, and either of the very large or very small carrier gas flow rates decreases the reduction rate. With using the smaller graphite particle size, the reduction rate is increased.

2. From the XRD patterns of the reduction products at different reduction stages for various temperatures, it is confirmed that reduction products of \( \text{Cr}_2\text{C}_3 \), \( \text{Cr}_7\text{C}_3 \), \( \text{Cr}_2\text{3C}_6 \) and Cr are produced in turn. The reduction contains various kinds of reactions such as direct reduction and indirect reduction of chromium oxide, the carbon solution loss reaction, the reduction of chromium oxide by various kinds of chromium carbide. From the X-ray pattern results, the reduction products are identified at various stages at different temperatures, and the relation among reduction products, reduction temperature and time has been characterized.

3. SEM observations and EDS analyses of the reduction products show that with the progress of carbothermic reduction of chromium oxide, the graphite particle is covered by the layer of reduction product of chromium carbides. It is deduced that at the initial stage of the reduction, direct reduction reaction dominates the reduction rate. Because the reduction rate become rather slow after the graphite particle is covered by the reduction product layer, the rate-controlling step should be CO/CO\(_2\) gas diffusion through the layer of the reduction products at the later stage of reduction.

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Fig. 13. SEM observation of pellets at different reduction stages.