Reduction and Desulphurization of Chromium Ore Pellet Containing Carbonaceous Material in the Flowing Atmosphere of H₂-CO*

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Synopsis

Chromium ore pellets containing carbonaceous material were reduced at various temperatures between 950 and 1350°C in the flowing atmospheres of H₂-CO with different H₂ concentrations. The rate of reduction increases to a large extent with the increase in H₂ concentration. In 100% H₂ atmosphere it is much higher than that in any other atmosphere investigated up to date. The kinetic analysis on the basis of a simplified reaction model showed that such promotion of reduction with H₂ is mainly due to the decrease in resistance of intraparticle diffusion of gaseous reactants and products through the reduced layer formed around chromite grain. The desulphurization during reduction of the pellet is remarkably promoted by the presence of a relatively low concentration of H₂ in furnace atmosphere. It seems that organic sulphur originated from coke is removed in the earlier stage of reduction and at lower temperatures whereas the sulphur removal from inorganic sulphide requires higher temperatures.

Key words: carbothermic reduction; desulphurization; chromium ore pellet; effect of furnace atmosphere; kinetic analysis; activation energy.

I. Introduction

Recently prereduction process of chromium ore pellet containing carbonaceous material has been developed in Japan,¹⁻³⁾ where the product has been used in an electric arc furnace to produce high carbon ferrochrome, furthermore it being intended as a charge in new production process of ferrochrome and chromium steel by the use of top and bottom blowing converter.⁴⁾

Fundamental researches⁵⁻¹⁸⁾ concerning carbothermic reduction of chromium ore have done in thermodynamic aspects, sequence of reduction, compositional and structural changes of chromite grain, effect of the types and the grain sizes of chromium ore and carbonaceous material and so on. However, there were few studies concerning effect of the gaseous composition of furnace atmosphere on the rate of reduction,¹⁹⁾ in spite of its great practical importance for improving operation of prereduction furnace. Thus, the authors²⁰⁾ have conducted the reduction tests of chromium ore pellet containing carbonaceous material in the flowing atmospheres of N₂-CO, N₂-CO-H₂ and N₂-CO-CO₂. The result showed that the rate of reduction increases with the decrease in the concentration of CO and with the increase in that of H₂ and that low concentration of CO₂ remarkably retards the progress of reduction and consumes the coke contained in pellet.

The present study was intended to highlight the promotion of reduction with H₂ in atmospheric gas. The pellet was reduced at various temperatures

between 950 and 1350°C in the flowing atmospheres of H₂-CO with different H₂ concentrations, kinetic analysis being conducted on the basis of an unreacted core model. In addition, experiments were conducted of effect of temperature and the H₂ concentration of atmospheric gas on desulphurization during reduction, some discussions on them being attempted.

II. Experimental

Chromium ore pellets containing carbonaceous material produced by Japan Metals and Chemicals Co., Ltd. were used. Their chemical composition is given in Table 1. Before using for reduction experiment, the pellets were ground by a polishing paper to about 0.87 cm in diameter and were dried at about 110°C. A basket made from nickel or molybdenum wire of 0.5 mm in diameter was used as a sample vessel.

As shown in Fig. 1, the reduction apparatus consisted of a thermobalance using a silica spring. The reaction tube was of high alumina and 3 cm in inner diameter. The tower containing copper powder was maintained at about 250°C for O₂ removal from CO.

When the furnace temperature was elevated to the required level, the pellet was suspended at the lower part of glass tube, the tube being closely connected to the reaction tube. The H₂-CO mixture with the required H₂ concentration was flowed through the reaction tube at the total flow rate of 400 Ncc/min. When the pellet was lowered along the axis of the tube, it was preheated first for 3 min at the place corresponding to 800~900°C and next for 2 min at the highest temperature zone. Thereafter, elongation readings of silica spring were taken by a cathetometer and were usually continued for 120 min.

The degree of reduction (*R*) was determined from the following equation:

$$R(\%) = \left[\frac{(L_t - L_e)(W - B)}{L_e - L_0} + B - B' \right] \frac{100}{A} \quad \dots\dots\dots(1)$$

where, *L*₀, *L*_{*t*}, *L*_{*e*}: elongation readings of silica spring at the beginning, at a given time and at the end of measurement, respectively

W, *B*: weight losses of the pellet after the end of measurement and pre-

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Table 1. Chemical composition of chromium ore pellet containing carbonaceous material. (wt%)

Cr ₂ O ₃	Fe	SiO ₂	Al ₂ O ₃	MgO	C	Ig. loss*
37.42	10.61	7.62	8.48	11.76	14.73	3.66

* At 900°C under N₂ atmosphere.

(1) CO gas	(11) Electric furnace
(2) H ₂ gas	(12) Reaction tube
(3) Needle valve	(13) Brass cap
(4) Flow meter	(14) Pellet
(5) Copper powder	(15) Pt-Pt-13%Rh thermocouple
(6) NaOH	(16) Glass tube
(7) Silica gel	(17) Silica glass spring
(8) P ₂ O ₅	(18) Centering ring
(9) Mg (ClO ₄) ₂	(19) Windlass
(10) To rotary pump	(20) Gas outlet

Fig. 1. Reduction apparatus.

heating (%)

B': volatile matter content of the pellet (%)

A: weight loss corresponding to the complete reduction of Cr and Fe oxides contained in the pellet. It was stoichiometrically calculated in which gaseous product was assumed to be CO only.^{17,20)}

Sulphur content of the pellets reduced under various conditions was determined by the method according to JIS.²¹⁾

III. Reduction Kinetics

1. Results

Reduction experiments were conducted over the temperature range of 950 to 1 350°C in the flowing atmospheres of H₂-CO with different H₂ concentrations. Several examples of reduction curves are shown in Figs. 2 to 5.

As shown in the figures, the rate of reduction increases with the increases in temperature and H₂ concentration of atmospheric gas. Effect of the H₂

concentration on the rate of reduction is more remarked, especially below 1 250°C. For example, the degree of reduction attained after 60 min at 1 100°C is only about 8 % in CO atmosphere, whereas it reaches much higher level of 52 % in 90% H₂-10% CO atmosphere. The reduction does not complete even after 120 min at 1 350°C with CO and 60% H₂-40% CO mixtures, whereas with 90% H₂-10% CO mixture it reaches to completion of reduction in about 60 min at the same temperature. The rate of reduction in H₂ atmosphere is much higher than that in any other atmosphere. The degree of reduction of more than 100 % observed at the later stage of reduction at 1 200°C or above is considered to be due to the contribution of reduction of other oxides such as SiO₂.

In order to examine the effect of H₂ concentration in more detail, the degrees of reduction attained after different durations of reduction at 1 200°C were plotted against the H₂ concentration in Fig. 6. It is found that the promoting effect with H₂ is remarkably large, especially in the ranges of H₂ concentration below 10 % and above 95 %.

2. Mainly Rate-determining Process and Applied Kinetic Equation

The reduction of chromium ore-carbon pellet involves the simultaneous progress of gaseous reduction of chromite grain and the Boudouard reaction. In addition, it involves the evolution of gaseous product mainly consisted of CO from the pellet into furnace atmosphere. Therefore, it may be rate-determined by the following processes:

- (1) Gas transfer between the surface of pellet and bulk gas.
- (2) Gas transfer through the pores present in pellet.
- (3) Gaseous reduction of chromite grain, including intraparticle diffusion of gaseous reactants and products, solid diffusion and interfacial chemical reaction.
- (4) Reaction of carbon grain with CO₂ and H₂O, including intraparticle diffusion of gaseous reactants and products and surface chemical reaction.

Of the above processes, the resistances of processes (1) and (2) may be neglected because it was observed in the previous study²⁰⁾ that the rate of reduction is almost independent of the flow rate of atmospheric gas and pellet diameter. Furthermore, it was also found that the resistance of process (3) is much larger than that of process (4).^{20,22,23)} Therefore, the process (3) was considered to be mainly rate-determining process in the reduction of chromium ore pellet containing carbonaceous material, so that kinetic analysis was conducted on this basis.

Since the reduction of chromite grain proceeds topochemically from the surface to the inside,¹⁸⁾ its rate may be described by the unreacted core model. According to this model, several kinetic equations including the resistances of various processes have been offered up to date.²⁴⁾ Here the kinetic analysis was conducted by the kinetic equation which includes the resistances of intraparticle diffusion and interfacial

Fig. 2. Reduction curves at different temperatures in the flowing atmosphere of CO.

Fig. 4. Reduction curves at different temperatures in the flowing atmosphere of 90% H₂-10% CO.

Fig. 3. Reduction curves at different temperatures in the flowing atmosphere of 60% H₂-40% CO.

Fig. 5. Reduction curves at different temperatures in the flowing atmosphere of H₂.

chemical reaction. The equation is given below²⁴⁾:

$$t = \frac{r_0^2 d_0}{6D_e(C-C_0)} [3-2R-3(1-R)^{2/3}] + \frac{r_0 d_0 K}{k_r(1+K)(C-C_0)} [1-(1-R)^{1/3}] \dots\dots\dots(2)$$

- where,
- t : reduction time (s)
 - r_0 : radius of unreacted chromite grain (cm)
 - d_0 : reducible oxygen concentration of chromite grain (mol/cm³)
 - C, C_0 : concentration of reducing gas at the surface of chromite grain and at the equilibrium stage (mol/cm³)
 - D_e : intraparticle effective diffusivity (cm²/s)
 - k_r : rate constant of chemical reaction (cm/s)
 - K : equilibrium constant (—).

Since the first and second terms in the right-hand side of Eq. (2) correspond to the times (t_D and t_k)

Fig. 6. Effect of the H₂ concentration of atmospheric gas on the degree of reduction attained after different duration of reduction at 1200°C.

which are taken by the resistances of intraparticle diffusion and interfacial chemical reaction, respectively, the overall reduction time (t) is expressed by the following equation:

$$t = t_D + t_k \dots\dots\dots(3)$$

Dividing the both sides of Eq. (2) by $[1 - (1 - R)^{1/3}]$, the following equation is derived:

$$t/F = A(3F - 2F^2) + B \dots\dots\dots(4)$$

where, $F = 1 - (1 - R)^{1/3}$

$$A = r_0^2 d_0 / 6 D_e (C - C_0)$$

$$B = r_0 d_0 K / k_r (1 + K) (C - C_0).$$

It has been found that the spinel components of chromite mineral contained in chromium ore is reduced roughly in the sequence $\text{Fe}_3\text{O}_4 \rightarrow \text{FeCr}_2\text{O}_4 \rightarrow \text{MgCr}_2\text{O}_4$.^{15,17)} Since the Fe_3O_4 component was little contained in the pellet investigated, the kinetic analysis was conducted concerning the reduction stage of FeCr_2O_4 component, in which the degrees of reduction to be used were determined by the division of the observed values of R by the degree of reduction corresponding to complete reduction of FeCr_2O_4 component.

3. Results of Kinetic Analysis and Discussion

Figures 7 and 8 illustrate the plots of t/F against $(3F - 2F^2)$ according to Eq. (4). At a temperature of 1 150°C or above, good linear relationship between them holds except for the later stage of reduction of FeCr_2O_4 component in which the contribution of solid diffusion is necessary to be taken into account. At a temperature of 1 100°C or below, however, the rate of reduction does not obey the above kinetic equation in any atmosphere investigated. This seems to be due to the fact that the reduction of FeO preceded that of Cr_2O_3 in the reduction stage of FeCr_2O_4 component, because Cr_2O_3 is hard to be reduced below 1 100°C.^{16,17)} As shown in Fig. 7, the line from regression of plots of t/F against $(3F - 2F^2)$ concerning the data of reduction in CO atmosphere gives a negative intercept with the ordinate. The reason is probably attributed for the reduction in this atmosphere to be rate-determined only by the intraparticle diffusion of reacting gases through the reduced layer of chromite grain.²⁰⁾

Apparent intraparticle diffusivities D_e ($=1/A$) and apparent rate constants of interfacial chemical reaction k_r ($=1/B$) were determined from the slopes and the intercepts of the lines from regression, respectively and were shown in Figs. 9 to 11 as functions of $1/T$ and the H_2 concentration of atmospheric gas, compared with the D_e and k_r values obtained in the previous study²⁰⁾ where the same pellet was reduced in flowing $\text{N}_2\text{-CO-H}_2$ atmospheres. The k_r value depends on the total concentration of H_2 and CO , but it is independent of the H_2 concentration except for reduction in the atmosphere with less than 10 % H_2 . Temperature dependence of k_r is substantially equal to each another, irrespective of the $\text{H}_2 + \text{CO}$ and H_2 concentrations of atmospheric gas. Apparent activation energy of interfacial chemical reaction ranges from 50 to 62 kcal/mol and is similar to that obtained in the hydrogen reduction of chromic oxide pellet,²⁵⁾ taking account of temperature dependence of the reaction-driving force $(C - C_0)$.

Fig. 7. Plot of t/F against $3F - 2F^2$ for the data obtained at 1 200°C in the flowing atmospheres of $\text{H}_2\text{-CO}$ with different H_2 concentrations.

Fig. 8. Plot of t/F against $3F - 2F^2$ for the data obtained at different temperatures in the flowing atmosphere of 60% $\text{H}_2\text{-40% CO}$.

The D_e values increase with the increase in H_2 concentration and its degree of increment is much larger, especially in the concentration range of less than 10 % H_2 . Temperature dependence of D_e decreases with the increase in H_2 concentration and hence apparent activation energy of intraparticle diffusion ranges from 51 kcal/mol for 100 % H_2 atmosphere to 120 kcal/mol for 10 % H_2 . It is noted that the temperature dependence is much larger than that observed in the gaseous reduction of iron oxide pellet.²⁶⁾ This seems to be due to the fact that the diameter and the fraction of pore formed in reduced layer of chromite grain change to a large extent with increasing temperature. In practice, the same tendency has been also observed in the hydrogen reduction of iron chromite and chromic oxide pellets.^{25,27)}

The above results of kinetic analysis showed that the H_2 in atmospheric gas promotes to a large extent the intraparticle diffusion of reacting gases but it

Fig. 9. Temperature dependence of k_r' .

Fig. 10. Temperature dependence of D_e' .

Fig. 11. Effect of the H_2 concentration of atmospheric gas on D_e' and k_r' .

has little effect on the interfacial chemical reaction. Since the diffusivity of H_2 - H_2O system is about eight times only as large as that of CO - CO_2 system, the promotion of intraparticle diffusion can not be attributed only to larger diffusivity of H_2 -containing atmosphere (H_2 - CO - H_2O - CO_2), especially in lower H_2 concentration and it is necessary to take any other effect into account. One of such effect is considered as shortening of the actual distance where CO and CO_2 diffuse mutually, owing to the progress of the reaction $H_2O + CO = H_2 + CO_2$ in the reduced layer of chromite grain.²⁸⁾

As mentioned earlier, solid diffusion in the interior of chromite grain contributes to a large extent to the overall reduction in the later stage of reduction of $FeCr_2O_4$ component. From analogy with this tendency, it is concluded that the reduction of $MgCr_2O_4$ component is mainly rate-determined by the solid diffusion.

IV. Desulphurization Behavior

1. Results

Sulphur content of the pellets reduced under various conditions was determined and the degree of desulphurization was calculated from the following equation:

$$D_s = 100 (\%S)_t (1 - f) / (\%S)_0 \dots\dots\dots (5)$$

where, $(\%S)_t$, $(\%S)_0$: sulphur contents of reduced and unreduced pellets, respectively

f : fractional loss in weight (—).

Figure 12 shows the changes in sulphur content and the degree of desulphurization during the reduction at 1 200 and 1 300°C in the flowing atmosphere of 20% H_2 -80% CO . The desulphurization proceeds at a higher velocity in the early stage of reduction and the degree of desulphurization of more than 80 % is attained after 40 min at 1 200°C and after 10 min at 1 300°C.

Figure 13 shows the effects of temperature and the H_2 concentration of atmospheric gas on the sulphur content and the degree of desulphurization. The sulphur content decreases in two steps below 1 150°C and between 1 200 and 1 250°C or 1 250 and 1 300°C and there is the corresponding stepwise increase in the degree of desulphurization. The desulphurization is remarkably promoted by the H_2 in atmospheric gas, especially in the concentration range of less than 20 % H_2 .

2. Discussion

The promotion of desulphurization with H_2 may be attributed to the fact that the reaction $H_2 + (S) = H_2S$ proceeds in preference to the reaction $CO + (S) = COS$ from a thermodynamic viewpoint. Figure 14 shows the relationship between equilibrium $P_{H_2S} / (P_{H_2S} + P_{COS})$ ratio and the H_2 concentration of atmospheric gas, providing that only H_2S and COS are produced as gaseous products containing sulphur.

Fig. 12. Desulphurization curves at 1200 and 1300°C in the flowing atmosphere of 20% H₂-80% CO.

Fig. 13. Effect of temperature and the H₂ concentration of atmospheric gas on sulphur content and the degree of desulphurization (reduction time: 120 min).

Fig. 14. Relationship between equilibrium $P_{H_2S}/(P_{H_2S} + P_{COs})$ and the H₂ concentration of atmospheric gas.

The equilibrium ratio increases with the increase in the H₂ concentration, and it amounts to more than 80 % at 20 % H₂. This makes clear for a relatively low concentration of H₂ to promote the desulphurization.

Sulphur contained in the pellet originates mainly from coke, in which most of sulphur is present as organic sulphur compound dissolved in carbon and

inorganic sulphide such as FeS and CaS.²⁹⁾ According to Neuhaus *et al.*³⁰⁾ the former ranges from 66 to 80 % of total sulphur content and is more easily removed than the latter.

From the consideration of the present result on the basis of the above information, it is concluded that the organic sulphur was removed in the early stage of reduction and at a lower temperature and that the sulphur removal from inorganic sulphide took place above 1200°C but in the H₂-containing atmosphere it did to a considerable extent even below 1200°C.

V. Conclusion

The reduction rate of chromium ore pellet containing carbonaceous material increases to a large extent with the increase in H₂ concentration of furnace atmosphere. In 100 % H₂ atmosphere it is much higher than that in any other atmosphere investigated up to date.

The data were analyzed by the use of the kinetic equation which includes the resistances of intraparticle diffusion of reacting gas and interfacial chemical reaction, providing that the reduction of FeCr₂O₄ component is mainly rate-determined by the gaseous reduction of chromite grain among various processes involved. The resistance of interfacial chemical reaction depends on the total concentration of H₂ and CO but it is almost independent of the H₂ concentration. On the contrary, the resistance of intraparticle diffusion decreases remarkably with the increase in H₂ concentration. As a result, it is concluded that the promotion of reduction with H₂ is mainly due to the decrease in resistance of intraparticle diffusion of gaseous reactants and products through the reduced layer formed around chromite grain.

The desulphurization during reduction of the pellet is remarkably promoted by the presence of a relatively low concentration of H₂ in furnace atmosphere. It seems that organic sulphur originated from coke is removed in the earlier stage of reduction and at lower temperatures whereas the sulphur removal from inorganic sulphide requires higher temperatures.

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REFERENCES

- 1) K. Ichikawa, S. Ozawa, K. Ushiyama and M. Yamanaka: *Nisshin Steel Tech. Rep.*, (1972), No. 26, 78.
- 2) T. Ohta, H. Haga, K. Sugita, T. Toyota, K. Sasaki and N. Moritama: *Tetsu-to-Hagane*, **61** (1975), S41.
- 3) S. Yoneka, K. Sugita, Y. Kimura, T. Furui and M. Fukuda: *Tetsu-to-Hagane*, **61** (1975), S40.
- 4) H. Kajioka, H. Ishikawa, H. Katayama, M. Kuwahara and M. Fujita: *Trans. Iron Steel Inst. Jpn.*, **26** (1986), B192.

- 5) A. N. Morozov, S. S. Lisnyak and A. M. Belikov: *Stal in Eng.*, (1963), 119.
- 6) W. L. Hunter and D. L. Paulson: U.S. Bur. Mines, Rep. Invest. 6755 (1966).
- 7) N. A. Barcza, P. R. Jochens and D. D. Howat: *Electr. Furn., Conf. Proc.*, **29** (1971), 88.
- 8) L. B. McRae and F. K. Siebrits: Nat. Inst. for Metall., Rep. No. 1724 (1975), South Africa.
- 9) N. L. Woollacott and J. B. See: Nat. Inst. for Metall., Rep. No. 1950 (1978), South Africa.
- 10) R. H. Nafziger, J. E. Tress and J. I. Paige: *Metall. Trans. B*, **10B** (1979), 5.
- 11) V. Ya. Belogurov, L. M. Izrailev, V. S. Kudryavtsev, V. V. Ponomarenko and S. A. Pchelkin: *Steel in USSR*, (1972), 511.
- 12) V. S. Kudryavtsev, L. P. Kostenenko, L. F. Shchugareva, V. Ya. Belogurov and L. L. Zav'yalova: *Russian Metall.*, (1975), No. 6, 5.
- 13) W. J. Rankin: *Trans. Inst. Min. Metall., Sec. C*, **88** (1979), C107.
- 14) W. J. Rankin: *Arch. Eisenhüttenwes.*, **50** (1979), 373.
- 15) H. G. Katayama and A. Tanaka: *Tetsu-to-Hagané*, **60** (1974), 1289.
- 16) H. G. Katayama: *Bull. Jpn. Inst. Met.*, **16** (1977), 851.
- 17) H. G. Katayama and M. Tokuda: *Trans. Iron Steel Inst. Jpn.*, **20** (1980), 154.
- 18) H. G. Katayama, M. Tokuda and M. Ohtani: *Tetsu-to-Hagané*, **70** (1984), 1559.
- 19) H. G. Katayama: *Tetsu-to-Hagané*, **63** (1977), 207.
- 20) H. G. Katayama and M. Tokuda: *Tetsu-to-Hagané*, **71** (1985), 1607.
- 21) Japanese Industrial Standard, JIS G1215 (1982).
- 22) H. G. Katayama and M. Tokuda: *Tetsu-to-Hagané*, **71** (1985), 1094.
- 23) H. G. Katayama, M. Tokuda and M. Ohtani: *Tetsu-to-Hagané*, **72** (1986), 1513.
- 24) M. Tokuda, H. Yoshikoshi and M. Ohtani: *Trans. Iron Steel Inst. Jpn.*, **13** (1973), 350.
- 25) H. G. Katayama: *J. Jpn Inst. Met.*, **50** (1986), 993.
- 26) Y. Hara, M. Tsuchiya and S. Kondo: *Tetsu-to-Hagané*, **55** (1969), 1297.
- 27) H. G. Katayama: *Tetsu-to-Hagané*, **72** (1986), 396.
- 28) V. Croft: *Metall. Trans. B*, **10B** (1979), 121.
- 29) Iron and Steel Handbook, II: Ironmaking and Steelmaking, 3rd ed., ed. by ISIJ, Maruzen, Tokyo, (1979), 203.
- 30) H. Neuhaus, H. J. Langhammer, H. G. Geck and H. Schenck: *Arch. Eisenhüttenwes.*, **37** (1966), 1.