INFACON 7, Trondheim, Norway, June 1995
Eds.: Tuset, Tveit and Page
Publishers: FFF, Trondheim, Norway

KINETIC STUDY ON SOLID STATE REDUCTION OF CHROMITE PELLETS

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ABSTRACT

The kinetics and mechanisms of solid state carbothermal and CO reduction of chromite pellets were studied by thermogravimetric analysis (TGA) in the temperature range 1420 - 1595°C. The kinetic investigations indicated that the reduction rate increases with temperature and initial carbon content. Weight loss curves, optical and scanning electron microscopy as well as micro analyses of the partly reduced pellets, were used to establish the reduction mechanisms of the chromite pellets. The results show that the reduction process of the chromite pellets with carbon under Ar atmosphere can be described well by the unreacted core model, the product gas CO_2 diffusion through the product layer being the rate controlling step. For the reduction of carbon free as well as carbon containing pellets under CO atmosphere, the situation is more complicated. The product layers both in the pellets and in the chromite particles within the pellets were observed. The reduction extent of the chromite particles in the outer part of the pellets was bigger than that in the inner part of the pellets.

INTRODUCTION

Ferrochromium is one of the most important alloying materials used in the production of stainless and high-alloy ferritic steels. Nowadays, high-carbon ferrochromium is mainly produced in submerged-arc furnaces. Although the process has been intensively developed, there is still need to reduce the energy consumption and to improve the chromium yield in the process. In the electric submerged-arc process, reduction proceeds via different mechanisms in various reaction zones, due to large temperature gradients. Knowledge of the reaction mechanisms in each zone can provide a guidance for improving the reduction efficiency, getting better chromium yield and thus decreasing the energy consumption.

The mechanism of chromite reduction has been a subject of controversy for many years. Barzca *et al.* [1] claimed that the prereduction of chromite by solid carbon is controlled by carbon diffusion across the layer of the reaction product, whereas Rankin [2] suggested that it occurs via carbon monoxide which surrounds the spinel grains and penetrates the fissures. Using thermogravimetric data and chemical analyses of the resulting alloys, Algie and Finn [3] proposed three stages in the reduction of a Transvaal chromite ore (LG-6) at 1300°C: (1) reduction of ferric iron to ferrous iron, (2) reduction of ferrous iron to metallic iron, and

(3) reduction of trivalent chromium to metallic chromium. Recently, Soykan *et al.*[4] studied carbothermic reduction of the same chromite ore as Algie and Finn [3] at 1416°C. They proposed the reduction mechanism involving the following three stages: (1) reduction of iron cations (Fe^{3+} and Fe^{2+} ions) at the surface of the chromite to the metallic state during the initial stages, followed immediately by the reduction of Cr^{3+} to Cr^{2+}, (2) the reduction of Fe^{3+} ions to Fe^{2+} ions at the reaction interface between reduced and unreacted core by Cr^{2+} ions, which are diffusing toward the center of the particle, diffusion of Fe^{2+} ions toward the surface, where they are reduced to the metallic state, and (3) the reduction of Cr^{3+} and Cr^{2+} ions to the metallic state (after the iron has been completely reduced), leaving an iron- and chromium-free spinel, $MgAl_2O_4$.

Due to the complexity of the reduction mechanisms it is evident that the kinetic relationships should also be quite different for different stages of the reaction procedure.

EXPERIMENTAL METHOD

Materials

Raw pellets of Kemi chromite ore mixed with about 0, 2.9 and 5.1 wt% carbon were investigated. Carbon was added in the form of coke powder, and bentonite was used as the binding material. The compositions of the chromite pellets and the amount of total initial removable oxygen W_{ox} (only the chromium and iron oxides were regarded as the reducible components) are shown in Table 1.

TABLE 1. Chemical analysis of the chromite pellets.

PEL-LET	Cr2O3	SiO2	FeO	Fe2O3	MgO	Al2O3	CaO	TiO2	V2O5	MnO	NiO	S	C	Wox
1	41.21	4.55	17.42	4.98	10.55	12.67	0.58	0.48	0.11	0.29	0.11	0.001	0.03	18.39
2	39.52	4.66	17.18	5.14	10.39	12.24	0.58	0.48	0.13	0.27	0.11	0.05	2.9	17.85
3	38.66	4.58	16.91	5.43	10.13	11.98	0.58	0.46	0.12	0.26	0.11	0.08	5.1	17.61

Method and Procedure

A number of experiments were carried out by the thermogravimetric analysis (TGA), where pellets with different carbon contents were heated under Ar or CO atmosphere at different temperatures. The experimental apparatus is illustrated in Fig. 1.

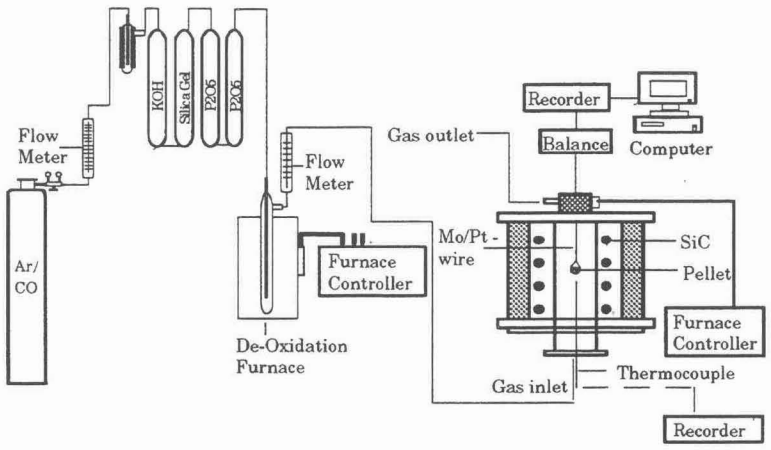

FIG. 1. Schematic Diagram of the Experimental Apparatus.

Reduction experiments were carried out at 1420, 1520 and 1595°C in a constant Ar or CO flow (2 l/min). In a typical test the pellet was first put in the upper part of the furnace, where the temperature (500~700°C) was low enough to avoid the reduction, but high enough to remove moisture and organic residuals. When the furnace reached the desired temperature, the pellet was slowly put down to the constant temperature zone. A PtRh30-PtRh6 thermocouple was installed just below the pellet to record the temperature of the reaction zone. In the experiments under CO, graphite crucible was used to maintain a high reducing atmosphere outside the pellet. The weight loss of the pellet was continuously recorded during the experiment. The weight loss values were used for the determination of the reduction degee R(t). For a carbon containing pellet reduced under Ar atmosphere, the reaction product is mainly CO at the present experimental temperatures and the reduction degree can be expressed as follows:

$$R(t) = X = \frac{W_0 - W_t}{W_{ox}} * \frac{16}{28} * 100\% \qquad (1)$$

where W_0 = weight of the sample at the beginning of reduction after the moisture removal
W_t = observed weight of the sample at time t during the reduction
W_{ox} = mass of the total initial removable oxygen

This formula is used later when discussing the reaction mechanisms.

EXPERIMENTAL RESULTS

Weight loss curves

The weight loss percentage was calculated from the equation:

$$\text{Weight loss, \%} = (W_0 - W_t) * 100 / W_0 \qquad (2)$$

Figs. 2, 3 and 4 show the weight loss curves of chromite pellets at 1420, 1520 and 1595°C under Ar or CO atmosphere and Figs. 5 and 6 weight loss curves of the pellets (0, 2.9 and 5.1 wt% carbon) at 1520°C under Ar and CO atmosphere, respectively. Fig. 7 shows the effect of atmosphere on the reduction of chromite pellet.

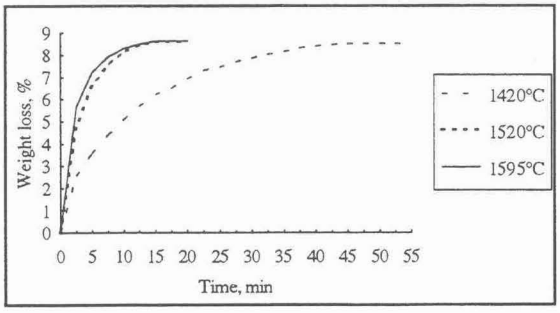

FIG. 2. Effect of temperature on reduction of chromite pellet (5.1 wt% carbon) under Ar.

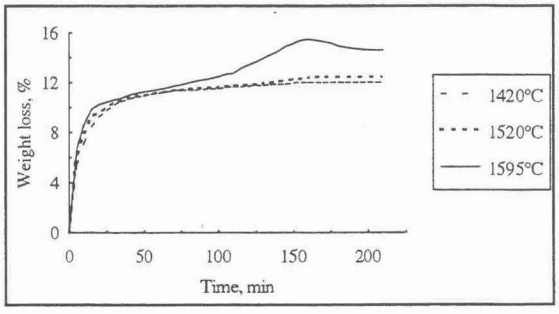

FIG. 3. Effect of temperature on reduction of chromite pellet (5.1 wt% carbon) under CO.

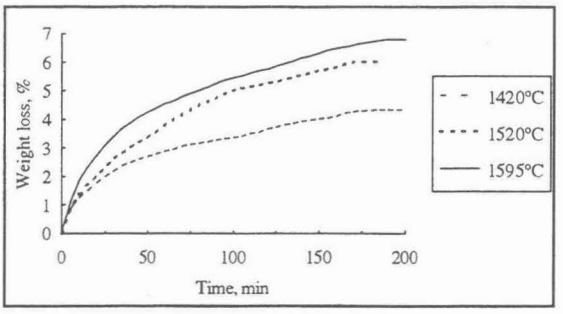

FIG. 4. Effect of temperature on reduction of carbon free chromite pellet under CO.

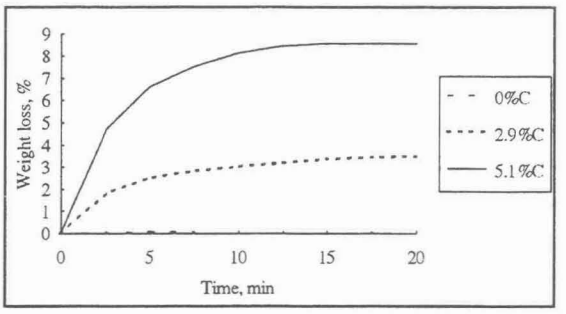

FIG. 5. Effect of initial carbon content on reduction of chromite pellet under Ar, T=1520°C.

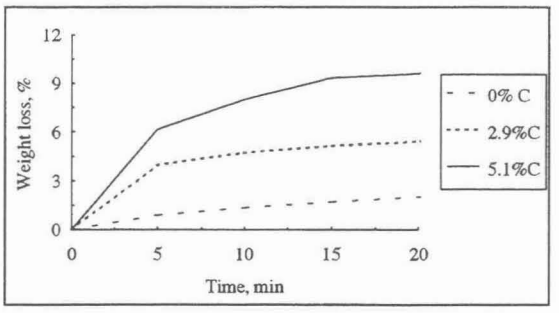

FIG. 6. Effect of initial carbon content on reduction of chromite pellet under CO, T=1520°C.

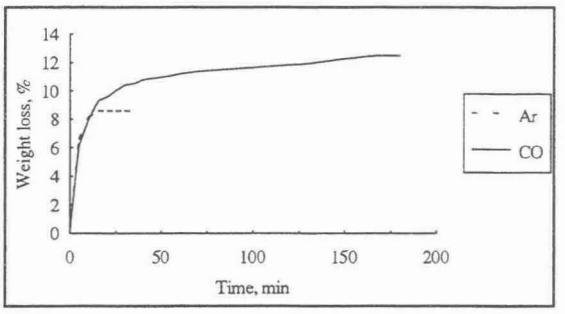

FIG. 7. Effect of atmosphere on reduction of chromite pellet (5.1 wt% carbon), T=1520°C.

Under Ar atmosphere, the chromite pellets were reduced by the solid carbon distributed inside the pellet. When the temperature increased from 1420 to 1520°C, the reduction rate increased significantly, but did not have any noticeable effect when further increasing the temperature to 1595°C (see Fig. 2). The final weight loss remained below the theoretical maximum weight loss, which is 11.9 if all carbon (5.1 wt%) is converted to CO.

As can be seen from Fig. 3, it seems that the effect of temperature on the reduction rate was not very prominent for the carbon containing pellets under CO atmosphere. After the carbon was consumed, the reduction continued with the aid of the external CO gas. This stage can be compared with the pure CO reduction shown in Fig. 4.

Figs. 5 and 6 show that the carbon mixed in the pellet has a great effect on the reduction rate. It should be noticed that the measured weight loss comprises of both the reacted carbon and the removed oxygen.

From Fig. 7 it can be seen that, at first the carbon in the chromite pellet has a dominant role in the reduction but after the carbon has been consumed, reduction of the chromite will continue with CO gas.

Optical photographs

Optical photographs were taken on a number of samples reduced under different conditions to obtain information on the structural changes of the pellets. Selected photographs are shown in Figures 8a to 8f.

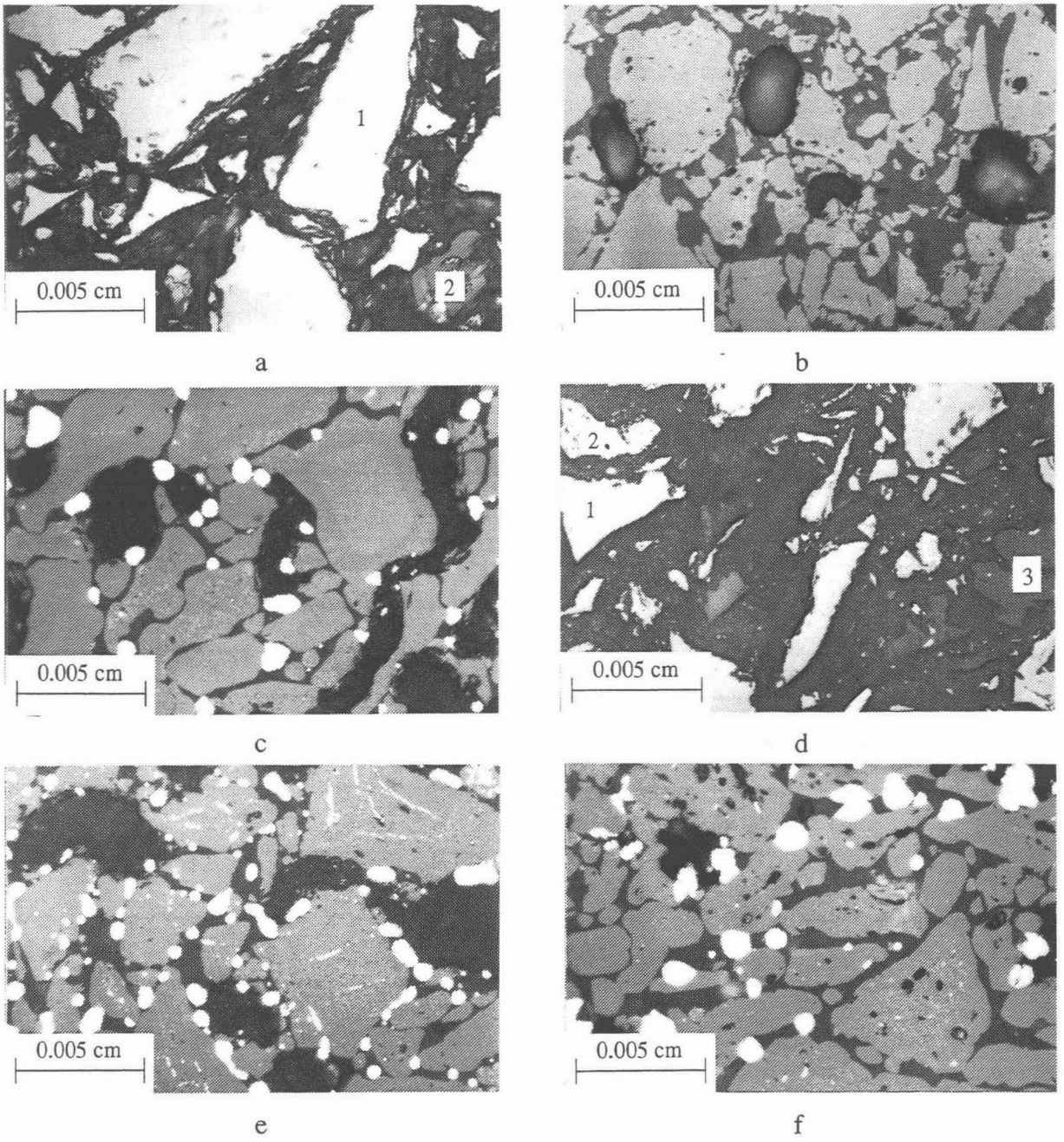

FIG. 8. (a) Raw pellet 0 wt% carbon (1 chromite, 2 silicate), (b) Carbon free pellet heated under Ar-atmosphere at 1520°C. (c) Carbon free pellet reduced under CO-atmosphere at 1420°C, (d) Raw pellet 5.1 wt% carbon (1 chromite, 2 graphite, 3 silicate), (e) Pellet 5.1 wt% carbon reduced under Ar-atmosphere at 1420°C, (f) Pellet 5.1 wt% carbon reduced under CO-atmosphere at 1420°C.

As can be seen from Fig. 8b, it is not possible to reduce carbon free chromite pellets under Ar-atmosphere (no metal particles were formed, pellet has only been sintered and silicate grains have melted a little bit), but when the atmosphere was changed to CO, the situation is different (see Fig. 8c). In addition to metal particles (white round areas), one can also see from Fig. 8c that chromite particles have two distinct zones - an inner zone, rich in iron, and an outer zone, where the iron content is much lower. In the case of carbon containing pellets, metal particles formed within the pellet can be observed, not only under CO (Fig. 8f) but also under Ar-atmosphere (Fig. 8e).

Microanalyses

In order to scrutinize the reduced pellet samples, the pellets were divided into three layers; the outer layer (1), the intermediate layer (2) and the inner core (3), which have been analyzed respectively. Selected analyses of metallic particles in different layers of the pellets are shown in Tables 2-4.

TABLE 2. Metal particles formed due to the reduction of the pellet with 5.1 wt% carbon under Ar at 1420°C.

LAYER	Fe	Cr	Al	Si	Ni	S
1	75.3	24.5	-	0.1	-	-
1	68.0	31.4	-	0.1	-	0.1
1	76.4	23.1	-	0.2	-	-
2	79.0	20.5	-	-	-	0.2
2	76.5	22.5	-	0.2	0.6	0.2
2	76.8	22.4	-	-	-	0.2
3	67.7	31.6	-	0.3	-	0.2
3	78.3	20.8	-	0.2	-	0.3
3	75.8	23.7	-	0.2	-	0.2

TABLE 3. Metal particles formed due to the reduction of carbon free pellet under CO at 1420°C.

LAYER	Fe	Cr	Al	Si	Ni	S
1	65.9	33.6	-	-	0.4	-
1	29.1	70.1	-	0.5	-	-
2	95.6	3.2	-	-	1.1	-
2	95.5	3.6	-	0.1	0.7	-
3	95.8	3.4	-	-	0.7	-
3	94.8	4.2	-	-	0.9	-

TABLE 4. Metal particles formed due to the reduction of the pellet with 5.1 wt% carbon under CO at 1420°C.

LAYER	Fe	Cr	Al	Si	Ni	S
1	75.7	23.6	-	-	0.4	0.2
1	76.6	22.6	-	-	-	0.3
1	78.8	20.4	-	-	0.5	0.2
2	80.5	18.2	-	-	0.5	0.8
2	85.9	13.3	-	-	0.4	0.4
2	86.3	12.9	-	0.1	0.6	-
3	73.1	24.1	1.4	0.4	-	0.7
3	79.2	19.6	0.4	0.5	-	0.3
3	81.6	17.8	-	-	-	0.2

As can be seen from Table 2, the composition of metal particles does not change much between the layers, but in the case of carbon free (Table 3) as well as carbon containing (Table 4) pellets under CO the situation is different. Especially from Table 3, the difference of the composition between particles in the different layers can be seen clearly. In the inner layer, it seems mainly iron oxides have been reduced, but in the outer layer, both iron oxides and chromium oxides have been reduced.

REDUCTION MECHANISM

According to the literature [2,5,6], the solid/solid-reaction between carbon and chromite proceeds through CO gas. Therefore, in the present work, the gas-solid reac-tion is considered to be the major reduction way. The reduction mechanism of chromite pellet under different conditions can be quite different. Here, only the reaction mechanism of carbon containing pellet under Ar at different temperatures will be discussed based on the experimental results of the weight loss curves, optical and SEM photographs as well as micro analyses of reduced pellets. The grain model developed by Sohn and Szekely [7] will be applied.

If we analyse the reduction process of the carbon containing chromite pellet in Ar, the possible steps of the solid - gas reaction taking place inside the pellets during the reduction process can be classified as follows:

(1) Boudouard reaction, including the gas transfer and the interface reaction with a carbon particle inside a pellet.
(2) Transfer of the gaseous reductant (CO) from the carbon surface to the surface of a near by chromite particle via the voids and through the gas film on the particle.
(3) Diffusion of the gaseous reductant through the porous product layer of the particle to the reaction interface.
(4) Adsorption of the gaseous reductant on the reaction surface, chemical reaction with the reducible oxygen in the lattice, as well as the desorption of the gaseous reaction product proceeding successively.
(5) Diffusion of the gaseous reduction product (CO_2) through the porous product layer to the carbon surface. Diffusion of the metallic iron and chromium and the cations and anions Fe^{3+}, Fe^{2+}, Cr^{3+}, Cr^{2+}, O^{2-} etc. in the chromite lattice depending on the reduction stage.
(6) Diffusion of the gaseous reaction product through the gas film around the chromite particle and via the voids to the outer gas phase of the pellet.

The reduction process will be controlled by the total resistance of the above six sub-processes combined in series. Katayama and Tokuda [8] concluded that the gas flow rate and the pellet diameter has very little effect on the chromite reduction rate, thus the sub-processes (2), (6) are not assumed to be the controlling step. In addition, the Boudouard reaction proceeds very rapidly at a high temperature and the reduction rate of chromite pellets with and without graphite crucible is the same (see Fig. 7.). Thus, the sub-processes (3), (4) and (5) might be the reduction rate controlling steps. In such a case, the grain model has the same form with the unreacted core model.

In order to simplify the model, the following assumptions have been considered:

(1) The chromite particle within the pellet has a spherical shape with unchangeable size.
(2) The rate of adsorption and desorption of the reaction gas on the chromite lattice is much faster than the chemical reaction rate.
(3) The diffusion of the cations Fe^{2+}, Cr^{2+}, Cr^{3+}, or anions O^{2-} as well as Fe, Cr are ignored.
(4) The gas diffusion in the particle product layer is equimolar counter diffusion. The diffusion of the reactant gas CO in the inward direction is easier than that of the product gas CO_2 in the outward direction through the product layer.

Therefore, the possible rate controlling steps can be the interfacial chemical reaction and/or the diffusion of gaseous product CO_2 in the product layer of the chromite particle. The reduction can be expressed in a general form:

$$CO + mMeO_x \rightarrow nMeO_y + CO_2 \quad (3)$$

$$C + CO_2 \rightarrow 2CO \quad (4)$$

The reduction model is schematically expressed in Fig. 9.

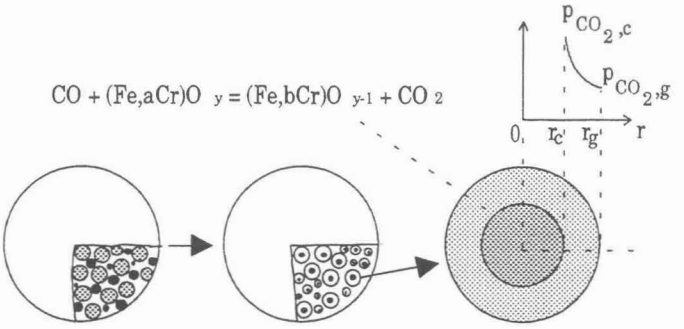

FIG. 9. Schematic diagram of the chromite reduction.

Control by Chemical Reaction

The overall rate is controlled by the rate of chemical reaction at the interface, when this is the principal resistance to the progress of reaction. The relationship between the reduction degree and the reduction time in this case is given by the following equation:

$$t_R = F(X) = 1-(1-X)^{1/F_p} \tag{5}$$

where
X = reduction degree
t_R = time of chemical reaction
F_p = particle shape factor (= 3 for spherical particles)

Control by Diffusion through Product Layer

When the chemical reaction at the interface presents a negligible resistance to the progress of reaction compared with diffusion through the product layer, the overall rate is controlled by the latter. The relationship between the reduction degree and the reaction time is given by the following equation:

$$t_D = t^*/\sigma_s^{\,2} = G(X) = 1-3(1-X)^{2/3}+2(1-X) \tag{6}$$

where
t_D = time of diffusion
t^* = dimensionless time
σ_s = the ratio of the rate of chemical reaction to the rate of diffusion

Overall Rate Determined by Both Chemical Reaction and Diffusion

If both the chemical reaction and the CO_2 diffusion in the product layer control the overall reduction rate, the relationship between the reduction degree and the reaction time is then given by:

$$t^* = F(X) + \sigma_s^2 G(X) \quad (7)$$

According to the experimental data, if the reaction time has a linear relationship with F(X), then $t_R = t^*$, the interfacial chemical reaction is the controlling step; if the reaction time equals to t_D , i.e, G(X) shows a linear function with time t^*, carbon dioxide diffusion through the porous product layer is the rate limiting step; otherwise, if $t^*/F(X)$ shows a linear change with the function $3F(X) - 2(F(X))^2$, then the reduction process has mixed control both by the chemical reaction and by the product CO_2 diffusion.

The experimentally determined kinetic data for the reduction of chromite pellets (5.1 wt% carbon) in the temperature range of 1420°C to 1595°C under Ar atmosphere were put into the equations (3), (4) and $t^*/F(X)$ versus $3F(X) - 2(F(X))^2$ and are shown in Figures 10 - 12.

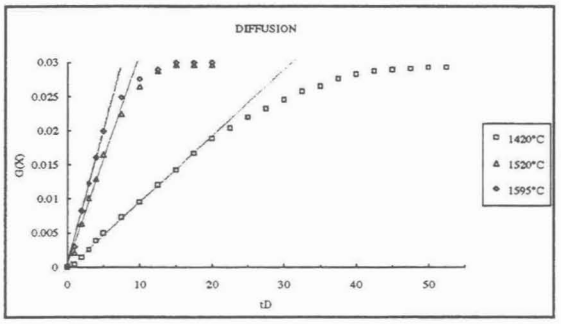

FIG. 10. Plots of G(X) versus t_D.

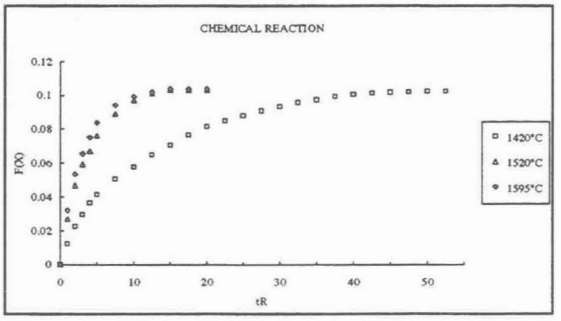

FIG. 11. Plots of F(X) versus t_R.

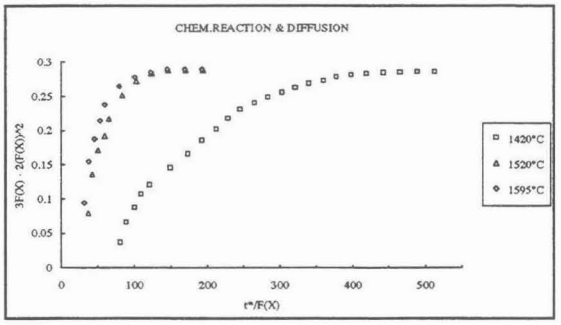

FIG. 12. Plots of $3F(X) - 2(F(X))^2$ versus $t^*/F(X)$.

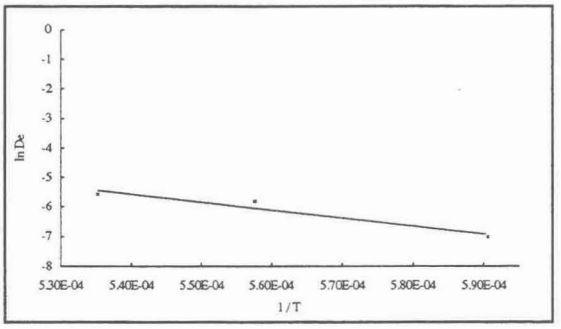

FIG. 13. Plot of ln D_e versus 1/T.

Since the plot of conversion function G(X) against t_D is a straight line at every temperature (at least most of the reduction time, see Fig. 10), it is concluded that diffusion of CO_2 through the product layer is the rate controlling step for temperature interval 1420-1595°C. In the later stage of reduction the plot tends to differ from a straight line because the reduction approaches the end due to the decreasing carbon content. The slopes of the curves in Fig. 10 can be considered as the effective diffusivity values (D_e) and are listed in Table 5.

TABLE 5. D_e values for the reduction of carbon containing chromite pellets under Ar, T = 1420 - 1595°C

TEMPERATURE, T K	$1/T*10^4$ K^{-1}	De min^{-1}	ln De
1693	5.91	0.000885	-7.030
1793	5.58	0.002979	-5.816
1868	5.35	0.003757	-5.584

Using the data in Table 5, the apparent activation energy for the reduction of carbon containing chromite pellets under Ar in the temperature range 1420 to 1595°C, can be obtained from the Arrhenius-type plot shown in Fig. 13. In the Arrhenius-relationship, $\ln D_e = \ln A - E_a / RT$, the activation energy E_a was calculated as 224 kJ/mol.

The reduction process of the chromite pellets with carbon under Ar can be described well by the unreacted core model. For the reduction of carbon free as well as carbon containing pellets under CO, the situation is more complicated. The product layers both in the pellets and in the chromite particles within the pellets were observed. The reduction extent of the chromite particles in the outer layer of the pellets is different from that in the inner layer of the pellets. The mechanisms will be discussed later.

CONCLUSIONS

The reduction kinetics of carbothermal and CO-reduction of chromite pellets in the temperature range of 1420°C to 1595°C were investigated in the present study. The experimental results showed increasing reduction rate with increasing temperature. The weight losses were, naturally, bigger in pellets with higher initial carbon content and under CO-atmosphere. By using the unreacted core model CO_2 diffusion in the product layer was concluded to be the rate controlling step in the reduction of chromite pellet with carbon under Ar atmosphere.

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