Isothermal Reduction Kinetics of Fe$_2$O$_3$ Mixed with 1–10% Cr$_2$O$_3$ at 1 173–1 473 K

Mohamed Hamdy KHEDR

Chemistry Department, Faculty of Science, (Beni-Suej branch) Cairo University, 57,103 St., Maadi P.O Box 41, Cairo Egypt.
E-mail: dkhedr@hotmail.com

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Fired pure and 1–10% Cr$_2$O$_3$-doped Fe$_2$O$_3$ compacts, were isothermally reduced with H$_2$ at 1 173–1 473 K. Compacts are prepared by mixing chemically pure powders of Fe$_2$O$_3$ and Cr$_2$O$_3$ in the required ratios then pressed at 30 kN into cylindrical form of compacts before being fired at 1 473 K for 20 hr. The characteristics of the prepared compacts have been studied using X-ray diffraction analysis technique and reflected light microscope. The isothermal reduction curves obtained showed that Cr$_2$O$_3$ has a significant effect on the rate of reduction of Fe$_2$O$_3$. From the apparent activation energy and the gas–solid mathematical formulations, the rate controlling step in the reduction process was determined and proved to be the interfacial chemical reaction at the initial stages, while at the final stages, a combined mechanism of solid-state diffusion and interfacial chemical reaction was the rate controlling step.

KEY WORDS: iron oxide; doping; Cr$_2$O$_3$; reduction; kinetics; hydrogen.

1. Introduction

For many years reduction has been carried out on the production of iron from its oxide ores. The influence of certain oxides on the course of reduction attracted the interest of investigators since iron oxide ores are seldom found not mixed with other metal oxides. Many investigators studied the reduction of iron oxides either individually or mixed with other oxides such as CaO, MgO and SiO$_2$ but small attention has been paid to the effect of Cr$_2$O$_3$ on the reduction of Fe$_2$O$_3$.

Chinje et al.$^{11}$ studied the gaseous reduction of Fe$_2$O$_3$–Cr$_2$O$_3$(30wt%) solid solutions at low oxygen potential to an iron-rich metal phase. Severe disintegration of pellets samples were accompanied by an evidence of the formation of a liquid phase at 1 083 and 1 233 K. The authors considered that this liquid may consist of ferrous chromite spinel (Fe–Cr–O) presumably containing chromous ions in equilibrium with an iron-rich metal phase.

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Reida et al.$^{3}$ studied the influence of alkali additions on the mechanism of joint reduction of oxides of iron and chromium. Investigation showed that the introduction of such addition to the mixtures of iron superconcentrate and chromium oxide intensifies the processes of the formation of (Fe,Cr)$_2$C$_3$, subsequently influencing all reduction stages.

Compounds of potassium increased the reactivity of the oxide mixture and reduced both the temperature of the initial reduction and also the energy of activation at each stage of the reduction process.

The mechanism of combined reduction of iron and chromium oxides in a Quasi-Binary oxide system was investigated by Popov et al.$^{4}$ Tests were conducted to study the phase change of products during the process of high-temperature synthesis of solid alloys obtained by reduction of iron and chromium-bearing oxide materials. Reduction proceeded through the formation of a carbide phase and its subsequent breakdown as a result of interaction with chromium oxide and finally a solid solution of chromium in iron is formed.

Many investigators studied the reduction of synthetic and natural chromite (which is mainly a mixture of Cr$_2$O$_3$ and Fe$_2$O$_3$). Sundarmurti et al.$^{5}$ studied the reduction of synthetic chromite with carbon. They found that the reduction of synthetic chromite by carbon is probably controlled by diffusion of oxygen to the surface in the initial stages of reduction leading to metalization of iron in the bulk. X-ray analysis of partially reduced samples (25% reduction degree) revealed the presence of FeCrO$_3$, Cr$_2$O$_3$, Cr$_3$O$_4$, Fe and excess graphite whereas no carbide formation was detected.

Rankin$^{6}$ studied the reduction of natural chromite–graphite mixtures, at temperatures up to 1 473 K, the reduction products were Fe, (Cr,Fe)$_2$C$_3$ and Fe$_3$C. The observed reduction sequences was consistent with thermodynamic considerations. Calculations showed that Fe and Cr$_2$O$_3$ formed at lower temperatures were metastable and would if permitted, eventually react with graphite to form Fe$_3$C and...
Cr$_7$C$_3$ respectively.

The present investigation is designated to study the effect of Cr$_2$O$_3$ 1–10 % by weight on the reduction behavior of Fe$_2$O$_3$ compacts at 1173–1473 K with H$_2$ gas. The microstructure of the partially and completely reduced compacts together with the kinetics data obtained from the reduction process were used to elucidate the reduction mechanism under isothermal conditions.

2. Experimental Procedure

Precalculated amounts of ≈250 mesh of Cr$_2$O$_3$ were mixed with Fe$_2$O$_3$ to prepare compacts having 1, 2.5, 5 and 10 % by weight Cr$_2$O$_3$. The blend was thoroughly mixed in an agate mortar then in a ball mill for two hours to ensure homogeneity and well distribution of the doped metal oxide in Fe$_2$O$_3$. The mixture was moistened with 10 % water, then equal weights of 1.5 g were pressed in a cylindrical mould of 7.5 mm inner diameter at 30 kN. The produced compacts were left overnight then dried at 393 K for 24 hr. The dry compacts were gradually heated in air in a tube furnace up to 1473 K and kept at this temperature for 20 hr. The fired compacts were left to cool gradually to avoid cracking due to thermal shocks.

The fired compacts (6.0 mm diameter and 9.0 mm height) were used for isothermal reduction experiments with 99.99 % purity H$_2$ gas using a previously described apparatus. Preliminary reduction experiments showed that the most suitable hydrogen flow rate required to ensure an adequate supply of gas and overcome the gas boundary layer diffusion resistance, thus avoiding the gas starvation is 1 l/min.

The fractional reduction is given by

\[
X = \frac{\text{Observed weight loss}}{\text{Total oxygen in Fe}_2\text{O}_3 + \text{Cr}_2\text{O}_3}
\]

The structural changes accompanying reduction of doped iron oxide compacts were examined by reflected light microscope and porosity measurements. The different phases formed during reduction were identified by X-ray diffraction technique.

3. Results and Discussion

3.1. Reduction Characteristics

Total porosity of fired pure and Cr$_2$O$_3$-doped Fe$_2$O$_3$ compacts was measured using Hg intrusion method and listed together with the different phases formed as identified by X-ray diffraction in Table 1. Data in the table indicates that Cr$_2$O$_3$ was not detected as a separate oxide but rather shared with some of the Fe$_2$O$_3$ for the formation of the phase (Fe, Cr)$_3$O$_4$ for all doping ratios in the range 1–10 % Cr$_2$O$_3$. It can be also noticed that total porosity significantly increased as the content of Cr$_2$O$_3$ in the Fe$_2$O$_3$ compact increased. Figure 1a) shows the microstructure of pure Fe$_2$O$_3$ in which a matrix of dense connected iron oxide with a relatively small number of micropores can be observed.

The addition of Cr$_2$O$_3$ as shown in Fig. 1b) for 10 % Cr$_2$O$_3$ doped Fe$_2$O$_3$ compact, causes an increase in macropores with a decrease in micropores. The oxide grains are less connected and separated by macropores which in turns imparts the compacts a relatively high total porosity values.

On the other hand, some grey patches representing (Fe, Cr)$_3$O$_4$ phase can be distinguished mostly at the neighbourhood of the macropores (Kirkendall effect).

The reduction curves of pure and doped compacts with pure H$_2$ at 1173–1473 K are given in Figs. 2a)–2e). In general it was found that temperature has a pronounced effect on the reduction of iron oxide. For each reduction curve, the rate of reduction was highest at early stage and gradually decreased with time till the end of the experiment (Arrhenius equation). For pure Fe$_2$O$_3$ the reduction extent attained 100 % for all reduction temperatures. On the other hand reduction was not complete by the addition of Cr$_2$O$_3$ and the reduction degree decreased with increasing amount of Cr$_2$O$_3$ and also with decreasing temperature this is because Cr$_2$O$_3$ remained unreduced at the end of the experiment. The corresponding relationships between the rate of reduction (\(dr/dt\)) at both initial (25 % reduction degree) and final (75 % reduction degree) stages and reduction temperatures are shown in Figs. 3a) and 3b). It is clear that the rate of reduction increased with increase of temperatures.

Figures 4a) and 4b) show the relationship between the rate of reduction (\(dr/dt\)) and the weight percent of Cr$_2$O$_3$.

<table>
<thead>
<tr>
<th>Content of Cr$_2$O$_3$ (%)</th>
<th>Content of (Fe,Cr)$_3$O$_4$ (%)</th>
<th>Total porosity (%)</th>
<th>Phase identified</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>0</td>
<td>6.2</td>
<td>α-Fe$_2$O$_3$</td>
</tr>
<tr>
<td>1.0</td>
<td>18.325</td>
<td>7.0</td>
<td>α-Fe$_2$O$_3$+ (Fe,Cr)$_3$O$_4$</td>
</tr>
<tr>
<td>2.5</td>
<td>19.5625</td>
<td>7.8</td>
<td>α-Fe$_2$O$_3$+ (Fe,Cr)$_3$O$_4$</td>
</tr>
<tr>
<td>5.0</td>
<td>21.625</td>
<td>11.0</td>
<td>α-Fe$_2$O$_3$+ (Fe,Cr)$_3$O$_4$</td>
</tr>
<tr>
<td>10.0</td>
<td>25.75</td>
<td>25.0</td>
<td>α-Fe$_2$O$_3$+ (Fe,Cr)$_3$O$_4$</td>
</tr>
</tbody>
</table>

Table 1. Total porosity and X-ray phase analysis of the fired compacts.

Fig. 1. Photomicrographs of fired compacts: a) Pure Fe$_2$O$_3$, b) 10 % Cr$_2$O$_3$-doped Fe$_2$O$_3$. 

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added at both initial and final stages respectively. It is clear that at the initial stages there was a decrease in the reduction rate by the addition of Cr₂O₃ up to 2.5% by weight then a very slight increase is observed up to 10% Cr₂O₃.

Table 2 shows the X-ray identifications for compacts containing 2.5% Cr₂O₃ partially and completely reduced at 1273 K. It is clear that rate of reduction of Fe₂O₃ is considerably higher than that for (Fe,Cr)2O₃ which is stable at initial stages and reduced only at final stages to Fe and Cr₂O₃.

Two factors seem to affect the rate of reduction of Cr₂O₃ containing compacts, these are the presence of the less reducible phase (Fe,Cr)₂O₃ and on the other hand the increased porosity by increasing Cr₂O₃ content which increase the possibility of reducing gas diffusion across solid pores to the reacting surface and consequently increases the rate of reduction. From Table 1 it is clear that the addition of Cr₂O₃ up to 2.5% causes an increase in the porosity from 6.2 to 7.8% which is a little bit small change, while the amount of the less reducible phase (Fe,Cr)₂O₃ is abruptly increased from 0 to 19.5625%, so up to 2.5% Cr₂O₃, the formation of the less reducible phase (Fe,Cr)₂O₃ is the predominant factor which retards the rate of reduction. On the other hand the increase of Cr₂O₃ up to 10% causes a significance increase in porosity from 7.8 to 25% while the amount of (Fe,Cr)₂O₃ increased from 19.5625 to 25.75%
which is a considerably less effective change.

For samples containing 1% Cr₂O₃, the amount of the phase (Fe,Cr)₂O₃ is 18.325 wt% while Fe₂O₃ is 49.5 wt%, so during reduction at the initial stages this amount of Fe₂O₃ was subjected to reduction creating a porous metallic iron (55% porosity) so samples containing 1% Cr₂O₃ caused an increase in the rate of reduction as a result of increasing porosity then a considerable decrease in rate is observed up to 10% reduction degree, this is attributed to the slow rate of reduction of the phase (Fe,Cr)₂O₃ and the non reducibility of Cr₂O₃ (Table 2).

3.2. Rate Controlling Mechanism

The apparent activation energy values have been calculated by many investigators in order to determine the rate controlling step. The general range of values that have been obtained by Strangway⁹) are summarized in Table 3.

To illustrate the rate controlling mechanism at both the initial and the final stages of reduction, the apparent activation energy (Eₐ) of reduction was calculated from Arrhenius equation;

\[ K_r = K_0 e^{(-E_a/R \cdot T)} \] ...............................(1)

The reaction rate constant (K_r) can be derived from a rate equation of the form:

\[ \frac{dr}{dt} = K_r p^n \] ...............................(2)

The relationships between the logarithm of the rate of reduction for pure and doped compacts and the reciprocal of the absolute temperature were plotted at both the initial and latter stages and presented in Figs. 5a) and 5b) respectively. The calculated values of the apparent activation energy obtained from these relationships are given in Table 4.

The calculated activation energy values indicate that the reduction process at the initial stages for both pure and doped compacts is controlled by the interfacial chemical reaction. On the other hand, at the latter stages of reduction, the solid-state diffusion (transport of metal from the points where oxygen is removed to points where nucleation and grain growth occur) contributed to the interfacial chemical reaction as a rate controlling mechanism. The mechanisms based on the magnitude of activation energy are not decisive but rather indicative.¹⁰)

For iron oxide pellets many reaction rate models were reported.¹¹–¹⁵) In the present work photomicrographs of partially reduced samples indicate that multilayers is the mode of structure formed during the course of reduction (Fig. 6), accordingly the grain model developed by Szekely¹⁶) was used for the analysis of the experimental results in this investigation. It assumes that a pellet is usually formed by compacting fine grains of the solid oxide. The overall shape may be approximated by that of a slab, long cylinder, or a sphere. Although the compacts in the present work are made of fine grains, but it is not easy to characterize the shape of the individual grains because they are usually of irregular shape and are distributed in size. For the convenient statement of the problem, the model considered the shapes of a sphere, long cylinder and flat plate for the pellets or the grains.

Thus, for the reduction of hematite with H₂ as a first
order reaction, the chemical reaction control formula is as follows,

$$\phi(X) = 1 - (1 - X)^{1/F} \quad \text{........................(3)}$$

where, $\phi(X)$ is the interfacial chemical reaction control conversion function.

The dimensionless parameters and conversion functions are based on the size and the shape of the grains. In the present investigation, the compact has a shape of cylinder whose length is 1.5 times as much as its diameter. Although these are not long cylinders, but the shape factor was taken as that of the cylinder and the grains are supposed to be long cylinders therefore $F_g$ was replaced by 2 in the above formula.

For more evidences, the mathematical formulae for gaseous diffusion, chemical reaction and mixed control were applied. Curves and not straight lines were obtained for the gaseous and mixed control mechanisms which confirm that neither is the rate controlling mechanism. On applying the formula of the interfacial chemical reaction control, i.e.,

$$\phi(X) = 1 - (1 - X)^{1/2} \quad \text{........................(4)}$$

it is obvious that during the initial stages reduction of pure and doped compacts at different temperatures, the relationship between $\phi(X)$ and $t$ is a straight line (Fig. 7a). This confirms that the interfacial chemical reaction is the rate controlling mechanism during the reduction of these compacts at the initial stages, while at the final stages a deviation is observed at high percent of reduction as shown in Fig. 7b. A photomicrograph of compact containing 2.5% Cr$_2$O$_3$ and reduced to 80% at 1273 K is shown in Fig. 8, it is clear that a wustite layer (W) is entrapped in metallic iron (I) and so the reducing gas could not diffuse through the layer, consequently solid-state diffusion of oxygen ions took place to allow further reduction and the mechanism of solid state diffusion contributes to the rate controlling mechanism at the latter stages of reduction for pure and Cr$_2$O$_3$-doped Fe$_2$O$_3$ compacts. This is in accordance with the calculated activation energy values.

4. Conclusion

(1) Pure Fe$_2$O$_3$ mixed with Cr$_2$O$_3$ and fired at 1473 K for 20 hr showed the formation of the phase (Fe,Cr)$_3$O$_4$

which caused the increase in porosity.

(2) Both temperature and addition of Cr$_2$O$_3$ showed a pronounced effect on the rate of reduction of Fe$_2$O$_3$.

(3) At the initial stages of hydrogen reduction a decrease in rate is observed up to 2.5% Cr$_2$O$_3$ then a very slight increase in the rate done up to 10%, the reduction process at this stage is controlled by the interfacial chemical reaction mechanism.

(4) At the final stages, the addition of 1% Cr$_2$O$_3$ causes an increase in rate of reduction then a decrease in rate is occurred by more addition up to 10%. The solid state diffusion mechanism contributed with the interfacial chemical reaction as the rate controlling mechanism at this stage.
Acknowledgment
The author is grateful to all members of Ironmaking lab. Extractive metallurgy Dept., CMRDI.

Nomenclature

\[ E_a : \text{the activation energy} \]
\[ K_r : \text{the rate constant} \]
\[ K_c : \text{the frequency factor} \]
\[ R_s : \text{the gas constant} \]
\[ T : \text{the absolute temperature} \]
\[ p : \text{the pressure of the reducing gas} \]
\[ n : \text{the order of reaction} \]
\[ \phi(X) : \text{the interfacial chemical reaction control conversion function} \]
\[ X : \text{the fractional reduction} \]
\[ F_g : \text{the grain shape factor} \]
\[ t : \text{the time} \]

REFERENCES


Appendix

For the fluid–solid reaction

\[ A_{(g)} + bB_{(s)} \rightarrow cC_{(g)} + dD_{(s)} \]

When chemical reaction is the rate controlling step, the overall rate can be expressed as the rate and disappearance of A by the surface chemical reaction as

\[ R_s = k [C_n^a - (C_n^a / K_e)] \] \hspace{1cm} (A-1)

\( R_s \) is the rate of reaction in mole of A per unit time per unit surface area of B.

\( n \) and \( m \) are reaction orders.

\( K_e \) is the equilibrium constant, \( k \) is reaction rate constant.

\( C_{A_n} \) is the gaseous reactant concentration at the reaction surface.

\( C_{C_n} \) is the gaseous product concentration at the reaction surface.

Sine resistance to gas boundary layer is negligible, then

\[ C_{A_n} = C_{A_n} = \text{concentration at the bulk gas stream}. \]

\[ C_{C_n} = C_{C_n} = \text{concentration at the bulk gas stream}. \]

Rate of reaction of A is equal to rate of disappearance of B

\[ i.e. \]

\[ hR_s = - \frac{dC_n^a}{dt} \] \hspace{1cm} (A-2)

where \( \theta_i \) is the molar density of solid B and \( r_s \) is the distance coordinate perpendicular to the solid surface.

Combining Eqs. (A-1) and (A-2) and rearranging in a dimensionless form then

\[ \frac{d\xi}{dt^*} = -1 \] \hspace{1cm} (A-3)

where

\[ \xi = \left( \frac{A_e}{F_g V_g} \right) r_s = \frac{r_c}{r} \] \hspace{1cm} (A-4)

\[ t^* = \frac{h k A_e r_s}{\theta_i A_e (F_g V_g) [C_{A_n} - (C_{C_n} / K_e)]} t \] \hspace{1cm} (A-5)

\( A_e \) and \( V_g \) are the original grain surface area and volume.

\( F_g \) is the shape factor.

\( r \) is the grain diameter of sphere or cylinder or slab thickness.

The extent of conversion \( x \) can be expressed in the following form

\[ X = 1 - \left( \frac{r_c}{r} \right)^{F_g} \] \hspace{1cm} (A-6)

i.e.

\[ \frac{r_c}{r} = \xi = (1 - X)^{1/F_g} \] \hspace{1cm} (A-7)

by integrating Eq. (A-3)

\[ \xi = 1 - t^* \] \hspace{1cm} (A-8)

Rearranging with Eq. (A-7)

\[ t^* = 1 - (1 - X)^{1/F_g} \] \hspace{1cm} (A-9)

Accordingly, the interfacial chemical reaction control conversion function \( Q(x) \) is defined as

\[ Q(X) = 1 - (1 - X)^{1/F_g} \]