RATE DETERMINING STEP IN THE GASEOUS REDUCTION OF PURE AND DOPED IRON OXIDES

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ABSTRACT

Pure wüstite, W1 (Fe$_{0.941}$O) and SiO$_2$-doped wüstite W2 micropellets (SiO$_2$-Fe$_{0.947}$O) were prepared by the non-isothermal reduction of Fe$_2$O$_3$ and 2.1 mass% SiO$_2$-Fe$_2$O$_3$ sintered compacts. The wüstite micro-pellets (250-150 μm) were characterized by XRD, specific surface area and their structures were examined with optical and scanning electron microscopes supported with Energy Dispersive X-ray analysis (EDX). W1 and W2 micropellets were isothermally reduced to metallic iron at 900-1100ºC with H$_2$, CO and their mixtures. The O$_2$-weight loss resulted from the reduction process was continuously recorded as a function of time. The influences of gas composition, temperature and total gas pressure (0.1 up to 1.0 atm) on the reduction rate were intensively studied and correlated to predict the corresponding reduction mechanism. The highest reduction rate (dr/dt) was obtained in H$_2$ and the lowest was in CO at their initial reduction stages. In H$_2$/CO gas mixture, the rate did not vary with gas composition in a simple manner. At final reduction stages, unlike in CO, a rate minimum was detected at 900-950ºC in H$_2$ and H2-rich gas mixtures which was attributed to α-γ Fe transformation. The presence of SiO$_2$ enhanced the reduction in CO and CO/H$_2$ mixtures. In H$_2$, a significant slowing down in the rate at later stages was noticed due to the presence of hardly reducible fayalite phase (Fe$_2$SiO$_4$). Iron carbide was identified in samples reduced by CO-containing gas mixtures. An incubation period was detected at lower temperature and increased with the decrease in PCO. The reduction mechanism was also proposed.
INTRODUCTION

Iron ores are converted into metallic iron in the blast furnace, which accounts about 95% of the world production. Direct reduction and smelting reduction processes are producing the balance. In most of direct reduction plants, iron oxides are reduced with reformed natural gas (H2/CO mixtures). DRI has gained a wide acceptance in electric arc furnace steel-making process, due to the decline in the availability of high quality scrap. In foundry industries, sponge iron is used in production of gray and ductile cast iron. The reduction of iron ores is a complex process involving a great number of physical and chemical variables. The structure and morphology of the intermediate oxides (magnetite and/or wüstite) are far from starting materials and have a great influence on the reduction kinetics. The presence of impurities usually associated with iron ores such as SiO2, CaO, MgO, Al2O3, MnO, etc., further complicates the reduction process [1, 2, 3]. Most of previous studies were dealt with one step reduction process (Fe2O3 → Fe), and scant attentions were given to the intermediate reduction steps. Recent publications [4, 5, 6, 7, 8] paid higher attention to the reduction kinetics and mechanism of the intermediate steps. The mechanism of reduction with CO is different from that with H2 and with H2/CO gas mixtures [9]. The presence of impurities promotes nucleation and grain growth of magnetite. The wüstite-iron transformation step is kinetically regarded as the most significant step, which controls the overall reduction process and different reduction models were proposed [10, 11]. Thus, the present investigation concerns with the reduction kinetics and mechanism of wüstite pure and SiO2 doped-wüstite micropellets at different reduction conditions.

METHODOLOGY

Chemically pure Fe2O3 and Fe2O3 doped with 2.1% SiO2 compacts sintered at 1350°C for 3hrs were prepared. Compacts were then partially reduced to wüstite in 60%CO-40%CO2 gas mixture at 1000°C till a constant weight loss was attained after which they cooled down in O2-free Ar gas to room temperature. The sintered compacts were crushed and 250+150µm size fraction was collected. The chemical formulae of pure wüstite is Fe0.941O, while that for and SiO2 doped-wüstite is Fe0.947O, which reported herein after as W1 and W2 respectively. The specific surface area of W1 and W2 are 0.0520 and 0.1218 m2/g respectively. The SEM photomicrographs of W1 and W2 are shown in Figure 1. It shows that, while W1 is dense and exhibited faceted plates, W2 is porous and contains macro pores due to the presence of fayalite (2FeO.SiO2) phase which counteracts recrystallization and sintering of micrograins.

Figure 1: SEM Photomicrograph of W1 and W2 micropellets (5000X)
W1 and W2 micropellets were isothermally reduced with purified H₂, CO and their mixture at 900-1100°C. The O₂-weight loss resulted from the reduction of wüstite to iron is continuously recorded as a function of time using a TGA analysis technique [12, 13]. The reduction was carried out at different total gas pressures (0.1-1.0 atm.). Partially and completely reduced samples are examined with optical (LM) and scanning electron microscopes (SEM). X-ray phase identification, total carbon analysis and surface area measurements (BET) techniques are also applied.

RESULTS AND DISCUSSION

Reduction Kinetics
The typical reduction curves of W1 and W2 micropellets at 900-1100°C with H₂ and/or CO were given elsewhere [18, 19]. Figure 2 (a, b) shows an example for the reduction of W1 and W2 micropellets 1000°C with H₂ and/or CO gas mixtures respectively. They show clearly that the presence of SiO₂ has a great influence in the behaviour during reduction which is also gas dependant.

![Figure 2: Typical Reduction curves of W1 (a) and W2 (b) at 1000°C](image)

The influence of total gas pressure of CO (P_CO = 0.1-1.0 atm) on the reduction behaviour of W1 micropellets at 1000°C is illustrated in Figure 3.
It can be observed that, unlike the reduction of W2, the reduction of W1 with CO, at lower \( P_{\text{CO}} \) pressures (< 0.5 atm.) clearly shows the presence of an incubation period and the reduction curve exhibited three distinct reduction zones as illustrated in Figure 4.

To highlight this phenomena more clearly, the relationship between the rate of reduction \((dr/dt)\) at the initial stages(5% extents) and the corresponding reducing gas composition is given in Figure 5.
The results showed that the rate of reduction gradually decreases with the increase in CO content in the gas mixture. In pure CO, an abrupt decrease in the rate was observed and this decrease decreases with rise in temperatures. This slowing down effect in the rate was eliminated in presence of 2.5%H₂ in H₂/CO. The influence of H₂ addition to CO on the rate of reduction (dr/dt) of W1 micropellets is shown in Figure 6.

In this experiment, the reduction of W1 was carried out with H₂/CO, H₂/CO and H₂/Ar. For the reduction with H₂ or with CO, a linear relationship between the rate of reduction, (R), and the H₂ content in the mixture, XH₂, followed the relationship;

\[
\ln (\text{R})_{\text{mixture}} = -A \times X_{\text{H}_2} + \ln (\text{R})_{\text{H}_2} \quad \text{at} \leq 2.5\% \text{ H}_2
\]  

where, A is a constant and (R)H₂ is the rate in pure H₂. This relationship is applicable at all temperatures and pressures. The reaction rate constant, K, is calculated from the relationship;

\[
R = KA \ P^n
\]

where; R is the rate of reduction (% sec⁻¹), A is the specific surface area (m².g.m⁻¹) and P is the pressure of reducing gas at a given temperature (atm.) n is the slope of line which gives
the order of reaction. In \( \text{H}_2 \) and \( \text{H}_2/\text{CO} \) mixtures, the value of \( n \) is almost 1.0 (± 0.05). In pure \( \text{CO} \), \( n = 1.23 \). The variation between the values of \( (K) \) and the gas composition is given in Figure 7.

\[ \text{Figure 7: Variation between reduction rate constant } (K) \text{ at initial reduction stages and gas composition at 1000°C} \]

It shows that the gas composition has greatly influence on the values of \( (K) \) depend on the wüstite composition. In \( \text{H}_2 \), the value of \( (K) \) for W1 is two times higher than W1, while in \( \text{CO} \), the value of \( (K) \) value of W2 is higher than that for W1. This is due to the presence of fayalite, which has a major influence of the rate of nucleation of iron.

The values of apparent activation energy values \( (E_a) \) for the reduction of W1 and W2 were computed from Arrhenius Equation [12]. Figure 8 shows the influence of gas composition on the \( (E_a) \) values calculated at 900-1100°C. It can be seen that the \( (E_a) \) values for W2 decreases gradually over the entire range of gases from 13.97 in \( \text{H}_2 \) to 6.78 kcal.mole\(^{-1}\) in \( \text{CO} \). For W1, the \( (E_a) \) values increases from 12.86 in pure \( \text{H}_2 \) to 21.35 kcal.mole\(^{-1}\) in 97.5%CO-containing mixture beyond which, an abrupt increases in its value resulting 32.09 kcal.mole\(^{-1}\) in pure \( \text{CO} \).

\[ \text{Figure 8: Influence of gas composition on the } (E_a) \text{ values activation} \]

The values of apparent activation energy at early stages, reveal several different rate controlling steps ranging from gaseous diffusion, interfacial chemical reaction and solid-state diffusion reactions. Under the present experimental reduction conditions, the reaction is most probably controlled by interfacial chemical at the initial stages since micropellets were used and the gas-boundary layer effect is eliminated. Also the solid state diffusion effect is negligible at the initial reduction stages. The wide scattering in \( (E_a) \) values (from
6.78 to 32.09 kcal.mole\(^{-1}\)) is resulted from the different pattern of nucleation and growths of iron on the oxide surface.

The SEM photomicrographs of 25% partially reduced W1 and W2 with H\(_2\) and CO are given in Figures 9 (a, b, c).

In W1, while the entire surface is covered by iron nuclei for the reduction with H\(_2\) (Figure 9a), the surface is partially nucleated with iron in pure CO (Figure 9b). Therefore, a higher value of (E\(_a\)) is expected in CO reduction than in H\(_2\) or H\(_2\)/CO mixtures. For W2 (Figure 9c), the surface is nucleated with iron nuclei, iron whiskers were formed through a combined effect of nucleation and growth on some active sites where fayalite (2FeO.SiO\(_2\)) is present. It has been reported that this phase is more easily reduced in CO than in H\(_2\), since H\(_2\) is unable to attack the regions where it is present [13].

The 75% reduced W1 and W2 at 1000ºC in CO are shown in Figure 10 (a, b). The surface of W1 (Figure 10a) is partially nucleated with iron and the grains is disintegrated resulting in large numbers of smaller grains. The surface of W2 is surrounded by dense iron layer along the entire surface of grains. The mechanism of grain disintegration in W1 is attributed to the carbon deposition and the secondary reactions [12, 13] resulting CO\(_2\) which entrapped in the grains till certain pressure (4-5 atm) after which the grains were disintegrated.

The influence of H\(_2\) on the initiation of reduction of W1 was examined by carrying out the reduction at 1000ºC in pure H\(_2\) up to 25% extent to develop iron nuclei on the grain surface, then replaced H\(_2\) by CO till the end. The results obtained were compared with those in pure CO from the beginning, as shown in Figure 11. It can be clearly seen that the presence of H\(_2\) is important at early stages to cover the oxide surface with iron nuclei which can be then enhancing the grain growth of these nuclei and speeding up the reduction process.
Incubation Period, Nucleation and Grain Growth

An important feature of the reduction of W1 micropellets with CO at lower pressures is the presence of an incubation period. It is interesting to mention that about 220 seconds incubation period was detected in the reduction with CO at 0.1 \( P_{CO} \). This period decreases with the increase in \( P_{CO} \). On the other hand, this incubation period was not observed in the reduction with \( H_2 \) or \( H_2 \)-containing gas mixtures. The formation of iron nuclei on the wüstite surface can take place by the removal of oxygen from oxide produces a local variation of the Fe/O ratio. After supersaturating is reached, the iron is separated out on the surface of wüstite in the form of nuclei. The iron formed is transported from the points where oxygen is removed to the points where nucleation and growth occur. This transport takes place through solid-state diffusion of iron along the surface. The number and distribution of iron nuclei depends upon the structural features of oxide (include lattice defects), the extent of grain boundaries and the foreign inclusions. The time required for the nucleation of metallic iron is quite dependent on the initial content of oxygen in the oxide. The quantity of oxygen removed in the nucleating period increases with increase of initial content of oxygen [15].

Mechanism of Reduction

The reduction with \( H_2 \) is characterized by the presence of initial rate constant up to certain extents depending on temperature and pressure, followed by a gradual decrease in the rate up to the end of reduction. The formed metallic iron is nucleated on the whole surface of wüstite grains. This indicates that the reduction reactions are not so complicated, since the \( (E_a) \) values are in the interfacial chemical reaction range. The reactions by which wüstite is reduced to iron may proceed as follows;

\[
(H_2)_g = (H_2)_{ads} \rightarrow 2H^+ + 2e^- \tag{3}
\]

\[
FeO \rightarrow Fe^{2+} + O^{2-} \tag{4}
\]

\[
2H^+ + O^{2-} \rightarrow (H_2O)_{ads} + (H_2O)_g \tag{5}
\]

\[
Fe^{2+} + 2e^- \rightarrow (Fe)_{nuclei} \tag{6}
\]
On the other hand, the reduction rate with CO was much slower at initial stages than that in pure H\textsubscript{2} and H\textsubscript{2}/CO gas mixtures at all temperatures and pressures. Moreover, the presence of incubation period is greatly retarded the reduction process. This evidence shows that the CO molecule is not directly reacted with FeO and it is most probably adsorbed on some active sites on the surface, then, reacted with wüstite to form intermediate carbonyl-like compound. After a while depending on temperature and P\textsubscript{CO}, this compound dissociates to metallic iron and CO\textsubscript{2}. The different reactions can be proposed as follows:

\[
\begin{align*}
(CO)\text{gas} & \rightarrow (CO)\text{ads} \\
FeO & \rightarrow Fe^{2+} + O^{2-} \\
(CO)\text{ads} + O^{2-} & \rightarrow (CO_{2})^{2-}\text{ads} \\
n (CO_{2})^{2-}\text{ads} + m Fe^{2+} & = [Fe_{m}(CO)_{n}]^{+} \rightarrow mFe + n(CO_{2})\text{ads} \\
(CO_{2})\text{ads} & \rightarrow (CO_{2})\text{gas}
\end{align*}
\]

For the reduction with H\textsubscript{2}/CO mixtures, it was found that the overall rate of reduction (R\text{mix.}) is non-additive and can not be obtained using a simple equation in the form:

\[
R_{\text{mix.}} = R_{CO} \cdot X_{CO} + R_{H2} \cdot X_{H2}
\]

Where R\textsubscript{CO} and R\textsubscript{H2} are the rates in pure CO and H\textsubscript{2} at the pressure corresponding in the gas mixture and X\textsubscript{CO} and X\textsubscript{H2} are the mole fractions of CO and H\textsubscript{2} respectively. The presence of small amount of H\textsubscript{2} with CO greatly increases the rate of reduction due to the increase in the number of iron nuclei on the wüstite surface. The addition of small amount of CO to H\textsubscript{2} greatly lowered the reduction rate compared with pure H\textsubscript{2}. This reduction mechanism is intensively discussed elsewhere [12, 13].

CONCLUSIONS

The highest rate of reduction was obtained in H\textsubscript{2} and decreases with the increase in CO content in the gas mixture. In pure CO, unlike in W\textsubscript{2}, the reduction of W\textsubscript{1} showed an abrupt decrease in the rate which increases in presence of ≥ 2.5% H\textsubscript{2}. In pure H\textsubscript{2}, the metallic iron was nucleated and covered the entire surface of W\textsubscript{1} even at the initial reduction stages. In CO/H\textsubscript{2} gas mixtures, the reduction rate is non-additive. In pure CO at lower pressures, an incubation period was obtained at initial reduction stages for W\textsubscript{1} which eliminated in presence of SiO\textsubscript{2}. At later reduction stages, the grains were disintegrated due to the carbon deposition and CO\textsubscript{2} evolved at high pressure. A correlation between the overall rate of reduction in CO/H\textsubscript{2} gas mixture and the rate in pure gases was developed.

REFERENCES


