Rate Controlling Step in the Reduction of Iron Oxides; Kinetics and Mechanism of Wüstite-Iron Step in H₂, CO and H₂/CO Gas Mixtures

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Abstract. Wüstite (W1 and W2) micropellets (150-50 μm) were prepared from the reduction of pure Fe₂O₃ and 2.1% SiO₂-doped Fe₂O₃ in 40%CO/CO₂ gas mixture at 1000°C which were then isothermally reduced in H₂, CO and H₂/CO gas mixtures at 900-1100°C. The reduction reactions were followed by Thermogravimetric Analysis (TG) technique. The effect of gas composition, gas pressure and temperature on the rate of reduction was investigated. The different phases formed during the reduction were chemically and physically characterized. In SiO₂-doped wüstite, fayalite (Fe₂SiO₄) was identified. At the initial reduction stages, the highest rate was obtained in H₂ and the lowest was in CO gas. In H₂/CO gas mixtures, the measured rate did not follow a simple additive equation. The addition of 5% H₂ to CO led to a measurable increase in the rate of reduction compared with that in pure CO. Incubation periods were observed at the early reduction stages of W₁ in CO at lower gas pressure (<0.25 atm). In SiO₂-doped wüstite, reaction rate minimum was detected in H₂ and H₂-rich gas mixtures at 925–950°C. The influence of addition of H₂ to CO or CO to H₂ on the reduction reactions, nucleation and grain growth of iron was intensively studied. Unlike in pure wüstite, the presence of fayalite enhances the reduction reactions with CO and CO-rich gas mixtures. The chemical reaction equations of pure wüstite with CO are given showing the formation of carbonyl-like compound [Feₙ(CO)ₘ]⁺. The apparent activation energy values, at the initial stages, ranged from 53.75 to 133.97 kJ/mole indicating different reaction mechanism although the reduction was designed to proceed by the interfacial chemical reaction.

1. Introduction

About 90% of iron and steel are produced by Blast Furnace–Basic Oxygen Furnace (BF-BOF) route and the balance is by Direct Reduction (DR) and Smelting Reduction (SR) routes. The BF-BOF route nowadays suffers from the high energy consumption and the CO₂ emission [1]. Great interest is now being devoted to increasing the iron production by Direct Reduction–Electric Arc Furnace (DR-EAF) process. New generation of DR process is recently developed to use coal, coal off -gases and coke oven gases as a source of heat and reducing agents [2-3]. The gaseous reduction of iron oxides is of practical importance, and more in-depth studies were carried out to understand the reaction kinetics and mechanism. The reduction of hematite (Fe₂O₃) to iron is a complicated reaction process due to the formation of lower solid oxides (magnetite and/or wüstite) prior to metallic iron. The experimental conditions have a paramount importance on the kinetic data which are influenced by the gases surrounding the reacting particles [4-5]. Most of previous studies were carried out with H₂ or CO [5-10] and scant attentions were paid to H₂/CO mixtures [7]. Below 570°C, hematite (Fe₂O₃) is reduced to
magnetite (Fe₃O₄) then directly to iron and above which, non-stoichiometric wüstite (Fe₁₋ₓO) is developed prior to iron. The composition of wüstite varies with temperature and the oxygen partial pressure in the gas phase. Although extensive works were done in the reduction of iron oxides directly to iron (Fe₂O₃ → Fe), the intermediate reaction steps (Fe₂O₃→ Fe₃O₄), (Fe₃O₄ → Fe₁₋ₓO) and (Fe₁₋ₓO → Fe) did not take such attention. The wüstite–iron transformation step is the most important step in the reduction process and determines the overall reaction rate and the degree of utilization of the reducing gases. In heterogeneous gas-solid reactions, the structure of the intermediate solid products plays significant roles on the reaction kinetics [4-5]. The rate of removal of O₂ from solids in the reduction reactions is a function of partial pressure of gases in the surrounding atmosphere and its activity of the oxide surface [8-10]. The magnitude of the dependence of the rate on the partial pressure is important to determine the order of reaction in the absence of inter-granular gas diffusion in porous product layer [4-11]. In previous studies by the author, Fe₂O₃, CaO-Fe₂O₃, and MgO-Fe₂O₃ compacts were reduced stepwisely at 900-1100°C to either; magnetite in CO/CO₂ then directly to iron in CO [12], or directly to wüstite in CO/CO₂ then to iron in CO [13], or to magnetite then to wüstite in CO/CO₂ and then to iron in CO [14]. The reduction mechanism from one step to another was predicted from correlations between the kinetics, grain structures and gas-solid mathematical model.

The present investigation aimed at studying the isothermal reduction behaviour of pure and SiO₂-doped wüstites at 900-1100°C in H₂, CO and their mixtures using micropellets to overcome the gaseous diffusion effects. The different factors affecting the reduction were intensively studied. The pattern of nucleation and the grain growth of metallic iron on the wüstite surface were used for better understanding the role of each gas in the mixture on the reduction reaction mechanism.

2. Materials and experimental technique

2.1 Materials

Analytical grades of Fe₂O₃ (99.5%) and 2.1% SiO₂-doped Fe₂O₃ compacts were made and sintered at 1250°C for 3hrs, then crushed to produce uniform size of micropellets (150-50μm). Pure Fe₂O₃ and SiO₂-doped Fe₂O₃ micropellets were isothermally reduced to wüstite in 40%CO/CO₂ gas mixture at 1000°C. The produced wüstites named herein as W1 and W2 respectively. The reducible O₂-content in W1 and W2 was measured from non-isothermal reduction tests of wüstites to iron in H₂ at 1100°C from which the oxygen content can be calculated. The chemical composition of W1 and W2 are Fe₀.₉₄₁O and Fe₀.₉₄₁O respectively. Wüstite compositions were also confirmed by XRF elemental analysis. Fig.1 (a) and (b) shows the morphologies and the grain structures of W1 and W2 respectively. Unlike in W1 where dense grains with faceted structure are formed, porous grains with parallel plates are formed in W2. The surface area of W1 and W2 are 0.0520 and 0.1218 m²/g respectively.

![Figure 1. SEM image for wüstite micropellet(a) W1 (b) W2 [5000X]](image)

X-ray diffraction shows the presence of well crystalline structure in W1 and the presence of fayalite and wüstite in W2. Fayalite is formed by the solid-state reaction between the freshly reduced wüstite and SiO₂: (2FeO + SiO₂ → 2FeO.SiO₂).

2.2 Reduction technique
The reduction of W1 and W2 micropellets in H₂, CO and H₂/CO mixtures was carried out isothermally at 900-1100°C. TG (STA-504, USA, accuracy = ± 1 μg) was applied for the continuous recording of the O₂-weight loss resulted from the reduction reactions. The schematic diagram showing gas purification system, reduction assembly and the gas pressure controller were given elsewhere [9]. At a given temperature, the extent of reduction at time (t) was calculated from:

\[ \%R_t = \left( \frac{W_{o} - W_t}{W_{o2}} \right) \times 100 \]  

Where: \( R_t \) is the reduction extent at a given time (t), \( W_o \) is the weight of wüstite micropellets, \( W_t \) is the weight of reaction product and \( W_{o2} \) is the total weight of the reducible O₂ in wüstite. In some tests, reduction was carried out at 0.1–1.0 atm. Partially and completely reduced products were examined by XRD, XRF, SEM, and RLM. The carbon content in the reduced products was also analysed.

3. Results and discussion

3.1 Reduction of pure wüstite (W1)

Figs. 2 (a) and (b) shows the reduction behaviour of W1 at 1000 and 1100°C respectively. At \( \leq 950°C \), the reduction in pure CO and in CO-rich gas mixtures (≥ 50% CO) was not completed and stopped at different extents. This is resulted from the thermal decomposition of CO, (reaction 2) and the rate of carbon deposition is higher than the rate of O₂-removal giving false recording in the weight-loss and was corrected from carbon analysis of the reduced samples. The highest rate of reduction was obtained in pure H₂ and the lowest rate was in pure CO. In CO/H₂ gas mixtures, the rate increases with rise with the increase in the H₂ content in the gas mixture. The reduction behaviour is generally characterized by almost constant rate up to certain extent depending on the applied temperature, followed by a gradual decrease in the rate at later stages. At ≥ 95% extents, the reduction in H₂ and H₂ rich gas mixture shows slowing down in the rate due to the sintering of metallic iron which hinder gas diffusion at the FeO/Fe interface and thus, the solid-state diffusion of Fe²⁺ and O²⁻ contributes in the reduction process. The higher the temperature, the higher sintering effect and the lower the reduction rate obtained. On the other hand, in CO and CO-rich gas mixtures; the slowing down in the rate at latter stages was eliminated due to the carbon deposition the subsequent reactions as follows:

\[ 2 (CO)_g \rightarrow 2 (CO)_{ads} \rightarrow (CO)_g + C_{gr} \]  

\[ 3 \text{Fe} + C_{gr} \rightarrow \text{Fe}_3\text{C} \]  

\[ 2 \text{FeO} + C_{gr} \rightarrow 2 \text{Fe} + (CO)_g \]  

\[ 3 \text{FeO} + 5 (CO)_{ads} \rightarrow \text{Fe}_3\text{C} + 4 (CO)_g \]  

\[ \text{Fe}_3\text{C} + 2 \text{FeO} \rightarrow 5 \text{Fe} + 2 (CO)_g \]

The CO₂ formed from reactions (4-6) may be partially entrapped and build up pressure at the FeO/Fe interfaces. With progress in reduction, the pressure of the entrapped gases increased up to certain level (4-5 atm) above which the particles are disintegrated giving large numbers of smaller micro-grains [15]. The newly formed FeO micrograins could further react with CO or with soot carbon to metallic iron and generate CO₂. The disintegration at the Fe₂/FeO interface retarded the sintering between metallic iron grains in the micropellets. Fig.3 (a,b and c) shows the structure of 75% reduced wüstite with H₂, 50%H₂/CO and CO gases respectively. It shows the formation of relatively larger and denser grains of iron in H₂ than that in H₂/CO mixtures. In pure CO, large numbers of small particles of iron are produced from the disintegrations at the FeO/Fe interfaces. The pattern of nucleation and grain growth of metallic iron on the wüstite surface at the early reduction stages was examined. Figs. 4 (a, b and c) shows SEM image in 25% reduced samples with H₂, 50%H₂/CO and pure CO respectively. In H₂, the wüstite surface is almost nucleated with iron showing small areas of the original wüstite surfaces (Fig.4 a). In 50%H₂/CO, relatively large areas of unreacted wüstite surfaces are also observed (Fig.4 b). In CO, iron is nucleated on small areas of wüstite surfaces showing higher grain growth (Fig.4, c). This indicated that gas composition has a great influence on
the mode of nucleation of iron on the wüstite surface and their grain growth. The presence of H₂ in the gas mixture enhanced the nucleation of iron on the entire surface of wüstite and the presence of CO accelerates the grain growth of the formed iron nuclei.

![Figure 2. Reduction path of W1 with H₂, CO and H₂/CO mixtures at; (a) 1000°C; (b) 1100°C](image)

![Figure 3. LM structure of W1, 75% extent at 1000°C in; (a) H₂ (b) 50% H₂/CO, (c) CO](image)

![Figure 4. SEM image of W1, reduced up to 25% at 1000°C in: (a) H₂; (b) 50% H₂/CO; (c) CO](image)

To investigate the effect of H₂ and CO contents in the gas mixture on the reduction, W1 was reduced at 1000°C at different total gas pressures. The total pressure of reducing gas was adjusted at 0.1 up to atmospheric pressure. Fig. 5 (a, b and c) shows the reduction path of wüstite micropellets in H₂, 50%H₂/CO and CO at different gas pressures respectively. It can be seen that, for a given gas composition, the rate of reduction increases with the increase in the total gas pressure. In CO, the reduction was delayed at the initial stages showing the presence of incubation periods at≤ 0.25 atm, (where no weight-loss was recorded). The measured incubation period increases with the decrease in P_CO as shown in Fig. 5 (c). Also, it was found that the reduction in pure CO is very low as compared with that in H₂ or even in H₂/CO gas mixture due to the difficulties of the formation of iron nuclei indicating that the reduction reactions of wüstites in H₂ are differed than that in CO.
Influence of total gas pressure on the reduction of W1 micropellets at 1000°C in:
(a) H₂; (b) 50% H₂/CO; (c) CO

Fig. 6 shows the variation between the rate of reduction of W1 calculated at different total gas pressure, while Fig. 7 depicts the variation between the rates calculated at 900-1100°C and the gas composition. It was found that the rates are gradually decreasing with the increase in the CO content in the gas mixture up to 5-10% H₂ containing gas mixture, below which an abrupt decrease in the rate was observed in pure CO. This indicated that the small addition of H₂ to CO in the mixture greatly promotes the nucleation of iron on the wüstite surface and consequently increases the rate of reduction.

In order to follow up the effect of the H₂ or CO in the gas mixtures on the reduction rate of wüstite, the following tests were adopted at 1000°C:

a- Role of H₂ in H₂/CO gas mixture; W1 was reduced in H₂ up to 25% extent, then H₂ was replaced by N₂. After a while, the reduction was continued to iron in pure CO. The reduction behavior of this test is given in Fig. 8 and compared with that in pure CO from the beginning. It can be observed that the reduction rate is greatly increased by nucleating the wüstite surface with iron in H₂. The nucleation of iron, at 25% extent, decreased the time of reduction from 40 min. in pure CO to 23 min. in H₂ followed by CO. This indicated that the presence of H₂ in gas mixture greatly accelerated the reduction of wüstite due to the easier formation of iron nuclei on the surface of wüstite which is subsequently grew up in the presence of CO gas.

b- Role of CO in H₂/Ar mixture; this was carried out by the reduction of wüstite in H₂, CO, H₂/CO and H₂/Ar gas mixtures. In gas mixtures, H₂ partial pressure was kept constant (P(H₂) = 0.25 atm) and CO or Ar are flowing at different partial pressure to adjust the total gas pressure as seen in Table 1. Fig. 9 shows the variation between the rate of reduction (dr/dt) at the initial stages in H₂, H₂/CO, CO and H₂/Ar and the gas composition respectively. The result obtained showed that, in pure H₂, H₂/Ar mixtures and CO, the rate decreases gradually in a linear relationship with the increase in P(H₂) or P(CO). On the other hand, the rate in H₂/CO gas mixtures showed non-linear relationship between (dr/dt) and...
gas composition indicating that the rate of reduction in H₂/CO gas mixtures did not obeyed the simple additive formulation in the form:

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

(7)

where: \( R_{CO}, \ R_{H2} \) are the rates in pure CO and pure H₂ at the pressure corresponding to the pressure of gas mixture, \( X_{CO}, \ X_{H2} \) are the mole fraction of CO and H₂ in the gas mixture. It is interesting to note that the \( \frac{d\theta}{dt} \) in pure H₂ and in H₂/Ar gas mixture are closer to each other indicating that the wüstite surface is saturated by H₂ molecules and Ar has no effect. The rates in H₂/CO mixtures are much lower than that in H₂ and H₂/Ar and the effect increased with the increase in CO mole% giving a higher effect in a gas mixture containing 25%CO and below which the effect is gradually decreased. This can be resulted from poisoning of the wüstite surface by CO molecules that prevent H₂ molecules to react with oxygen from wüstite.

**Table 1.** Variation between the \( P_{CO} \) in the mixture and the total gas pressure \( (P_{H2}=0.25\text{atm}) \)

| \( P_{H2} \) + PCO | (0.250 + 0.00) | (0.250 + 0.025) | (0.250+ 0.083) | (0.250 + 0.250) | (0.250 + 0.750) |
|-------------------|----------------|-----------------|-----------------|-----------------|-----------------|
| Pressure (atm)    | 0.250          | 0.275           | 0.333           | 0.500           | 1.000           |

\[ (\text{H}_2)_{\text{g}} = (\text{H}_2)_{\text{ads}} \rightarrow 2\text{H}^+ + 2e^- \]  

(8)

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

(9)

\[ 2\text{H}^+ + \text{O}^{2-} \rightarrow (\text{H}_2\text{O})_{\text{ads}} + (\text{H}_2\text{O})_{\text{g}} \]  

(10)

\[ \text{Fe}^{2+} + 2e^- \rightarrow (\text{Fe})_{\text{metal}} \]  

(11)

**3.1.1 Chemical reaction of pure wüstite micropellets.** Based on the reduction behaviour, pattern of nucleation and grain growth of iron at various gas pressure and the presence of incubation periods in CO at lower gas pressure, the chemical reaction wüstite in H₂ and CO can be presented as follows:

a) Reaction of wüstite with H₂:

\[ (\text{H}_2)_{\text{g}} = (\text{H}_2)_{\text{ads}} \rightarrow 2\text{H}^+ + 2e^- \]  

b) Reaction of wüstite with CO:

\[ (\text{CO})_{\text{g}} = (\text{CO})_{\text{ads}} \]  

(12)

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

(13)

\[ (\text{CO})_{\text{ads}} + (\text{O})^{2-} \rightarrow (\text{CO}_2)_{\text{ads}} \]  

(14)

\[ n (\text{CO}_2)_{\text{ads}} + m \text{Fe}^{2+} \rightarrow [\text{Fe}_m(\text{CO}_2)_n] \rightarrow m \text{Fe} + n (\text{CO}_2)_{\text{ads}} \rightarrow n(\text{CO}_2)_{\text{g}}. \]  

(15)

Where: \( n \) is the number of \( (\text{CO}_2)_{\text{ads}} \) molecules reacted with \( m \) molecules of \( (\text{Fe})^{2+} \) to produce the intermediate carbonyl-like compound which is subsequently dissociated to \( \text{Fe}_{\text{metal}} \) and \( (\text{CO}_2)_{\text{g}} \).

**3.2 Reduction of SiO₂-doped wüstite (W2)**

Micropellets of W2 were reduced with H₂, CO and H₂/CO mixtures at 900-1100°C. Fig 10 (a) and (b) shows the reduction path obtained at 1000 and 1100°C respectively. It can be seen that the rate of...
reduction, up to certain extent, increased with the increase in the H\textsubscript{2} content in the gas mixtures. The reduction with H\textsubscript{2} is characterized by an initial constant rate up to a certain extent followed by slowing down till the end of reduction.

\textbf{Figure 10.} Influence of gas composition on the reduction of W2 at; (a) 1000°C (b) 1100°C.

The reduction in pure CO shows a continuous decrease in the rate with progress in reduction. At \( \leq 1000\,^\circ\text{C} \), the reduction was stopped before completion due the higher rate of carbon deposition than the rate of oxygen removal from the reduction. In H\textsubscript{2}/CO mixtures, the rate increases with the increase in H\textsubscript{2} content in H\textsubscript{2}/CO mixtures. The SEM image of 25% and 85% reduced samples in H\textsubscript{2}, 50% H\textsubscript{2}/CO and CO at 1000°C are given in Figs. 11 and 12 (a), (b) and (c) respectively. The structure formed at 25% extent in H\textsubscript{2} and H\textsubscript{2}/CO mixture is characterized by the formation of numbers of hexagonal iron on the wüstite surface with well defined-triangular pores. While in pure CO (Fig.11 c), iron whiskers were formed, even at early stages of reduction. Iron whiskers were formed by the formation of smaller iron nuclei growing up in a direction perpendicular to the wüstite surface.

\textbf{Figure 11.} SEM image of 25% reduced W2 in; (a) H\textsubscript{2}; (b) 50%H\textsubscript{2}/CO; (c) CO [5000 X]

The structure developed at higher reduction extents in H\textsubscript{2} and H\textsubscript{2}/CO mixtures shows the formation of iron layer partially surrounding the wüstites grains as shown in Fig.12 (a, b). In CO, the reduction is characterized by the formation of dense iron layer surrounding wüstite surface forming entrapped wüstite relics as shown in (Fig.12 c). In this case, wüstite relics cannot be reacted directly with gases (H\textsubscript{2} or CO) and the solid-state diffusion are contributed in the reduction process.

\textbf{Figure 12.} LM microstructures of 85% reduced W2 in; (a) H\textsubscript{2} (b) 50%H\textsubscript{2}/CO (c) CO [320 X]

3.3 Reduction kinetics and mechanism
The nucleation and grain growth of iron on the surface of W1 and W2 in H\textsubscript{2}, H\textsubscript{2}/CO and CO differs and have a measurable influence on the reduction mechanisms. Moreover, the presence of even
smaller molar ratio of H₂ in H₂/CO mixtures promotes the reduction of pure wüstite. The role of either H₂ or CO in the gas mixtures was intensively studied and the morphology and the grain structure showed that W1 is dense than W2 due to the presence of fayalite (2FeO.SiO₂). From the reduction bath of W1 and W2, the reaction rate constants (K) were calculated from the relationship:

\[ R = K A P^n \]  

(16)

Where: \( R = \) rate of reduction (% sec\(^{-1}\)), \( A = \) surface area of wüstites (m\(^2\)g\(^{-1}\)), \( P = \) reducing gas pressure (atm) and \( n = \) order of reaction. The variation between K values and the gas composition of W1 and W2 are depicted in Fig. 13, from which the followings can be noticed:

(a) In pure H₂, the rate constant for W.II is approximately two times lower than that for W.I. This due to the presence of hardly reducible fayalite (7.8 %) in H₂ gas[16]. It is interesting to note that there are significant differences in the pattern of nucleation and growth of iron on the surface of W1 and W2. In W1, the entire surface is almost nucleated with iron whereas the surface of W2 grains is partially nucleated with a small numbers of iron grains since hydrogen is unable to attack the regions where fayalite is present. Thus the reduction is hindered giving lower rate of reduction in W2 than in W1.

(b) The reduction with CO shows that the rate constant (K) in W2 is about 3 times higher than that in W1. This could be due to the presence of fayalite phase which is easily reduced in CO rather than in H₂ [16]. Accordingly the reduction in CO would proceed on the regions of the grains surfaces where fayalite is present.

\begin{figure}
\centering
\includegraphics[width=0.8\textwidth]{figure13}
\caption{Variation between reaction rate constant (K) and the gas composition at 1000°C.}
\end{figure}

The apparent activation energy (Ea) for the reduction of W1 and W2 at 900-1100°C were calculated from Arrhenius equation [8] and the computed values are given in Table 2

\begin{table}
\centering
\caption{Apparent activation energy values (Ea) computed from Arrhenius plots at 900-1100°C}
\begin{tabular}{|c|c|c|c|c|c|}
\hline
\% H₂ + \%CO & W1 & W2 & \% H₂ + \%CO & W1 & W2 \\
\hline
100 & 0.0 & 53.75 & 58.39 & 25 & 75 & 75.65 & 35.53 \\
75 & 25 & 60.61 & 48.07 & 10 & 90 & 80.84 \\
50 & 50 & 64.79 & 41.8 & 5 & 95 & 89.24 \\
0.0 & 100 & 133.97 & 28.34 \\
\hline
\end{tabular}
\end{table}

For W1, as the CO content in the reducing gas mixture increases the Ea values gradually increases up to 95 % CO beyond which an abrupt increase in values were obtained. This indicates that the reduction of W1 is much easier in H₂ than that in CO. For W2, on the other hand, the Ea values gradually decrease with the increase in the H₂ content in the gas mixture indicating the easier reduction of W2 in CO than in H₂. This is resulted from the nucleation and grain growth of metallic iron on the wüstite surfaces as shown in Figs 3 and 11 for W1 and W2 at 25% reduction extents (Figs 4 and 11). The values of Ea obtained for W1 and W2 indicated several different rate controlling processes ranging from gas diffusion (≤30 kJ/mol) to interfacial chemical reaction (30-50 kJ/mol) and
to solid-state diffusion (≥80 kJ/mol). The measured overall reduction rate is not equivalent to the specific rate of chemical reaction but it also depends on the active surface area of the oxide and the diffusion coefficient of the reducing gas. Thus, the activation energy (Ea) obtained does not necessarily corresponding to the specific rate of chemical reaction but more reasonably to whatever process is controlling. In the present the followings conditions were considered to justify the rate controlling step in the reduction of wüstite to iron:

a) Micropellets (150 - 50µm) were used to minimize the resistance to gas diffusion in the intergranular pores. Accordingly, the gaseous diffusion effect can be minimized.

b) The reduction of wüstites was carried out directly to iron (one step reduction) to eliminate the complication arises from the formation of intermediate lower oxides.

c) At the early stages of reduction, the reduced metallic iron formed around the individual wüstite grains is very thin and consequently, the resistance to the solid state diffusion of Fe²⁺ and O²⁻ can also be neglected.

Under these conditions, the interfacial chemical reaction is most probably controlling the reduction of wüstite. The differences in the apparent activation energy values obtained could be related to the nucleation and the grain growth of iron and thus the Ea values cannot be taken as decisive evidence to predict the reduction mechanism but can be monitored to an indicative for the process.

4. Conclusions
The results obtained concluded the followings;

a) The rate of reduction increased with rise in temperature and with the increase in the H₂ content in the gas mixture. Small addition of H₂ to CO greatly accelerated the reduction rate, while the addition of CO to H₂ retarded the reduction process.

b) The nucleation of iron on the wüstite surface was dependant on the wüstitecomposition and its morphology. In H₂ and H₂-rich mixtures, iron is nucleated on the pure wüstite surface, while in CO, iron whiskers were formed in W₂ due to the presence of fayalite (2FeO.SiO₂).

c) The reduction of W₁ in H₂, H₂/Ar increased linearly with the increase in the H₂ content in the mixture. In H₂/CO gas mixtures, non-linear relation was obtained showing that the measured rate (dr/dt) is not additive.

d) The apparent activation energy values calculated for W₁ and W₂ showed two different trends. For W₁ the values gradually increased with the increase in CO content in the gas mixture up to 95% followed by an abrupt decrease in pure CO. For W₂, the Ea values were gradually decreased with the increase in CO content due to the presence of fayalite which promote the reduction in CO.

e) The reduction of W₁ and W₂ at the initial stages is most probably controlled by interfacial chemical reaction mechanism although the discrepancy in the values of Ea obtained. This is arises from the use of micropellets and the formation of thin film of iron on the wüstite surface at 5% reduction extent. The magnitudes of the apparent activation energy values could not be taken as a decisive conclusion but could be taken as an indicative approach for the rate controlling mechanism.

References
[1] Geerdes M, Toxopeus H and Vliet C 2009 “Modern Blast Furnace Ironmaking”, 2nd Edn 164, Delft . IOS Press BV.
[2] Chalttetjee A 2010 “Sponge Iron Production by Direct Reduction of Iron Oxide”, Textbook, PHI Learning Private Limited, New Delhi, P 353.
[3] Moussa EA, Senk D and Babich A 2010 Steel Res. Int. 81 (9), 706
[4] Bradshaw AV 1970 Trans IMM, 79, C281.
[5] Unal A and Bradshaw AV 1983 Met. Trans., 14B, 743.
[6] Shehata KA and Ezz SY 1973 Trans. Inst. Min. Met., Sec. C 82, 38.
[7] El-Geassy AA, Shehata KA and Ezz SY 1977 Trans ISIJ, 17, 629.
[8] El-Geassy AA 1986 J. of Mater Sci., 12, 3889.
[9] El-Geassy, Rajakumar V 1985 Trans ISIJ, 25, 449
[10] El-Geassy AA 1985 Trans ISIJ, 25, 1037
[11] Mousa EA, Omar AA, Nasr MI and El-Geassy 2007, Steel Res.Int., 78 (8), 579.
[12] El-Geassy AA 1997 J. ISJ Int. 37, 844-853.
[13] El-Geassy AA 1998 Scand. J. of Metallurgy, 27 (.5), 205-213.
[14] El-Geassy AA 1999 J. Ironmaking and Steelmaking, 26, (1), 41-52.
[15] Bohnenkamp K Riecke E and Engell HJ 1967 Arch Eisenhüttenw., 38, 240
[16] Mazanek E and Jasienecka S 1966 JISI, 204, 344.