

DIRECT REDUCTION OF ATTEPE IRON ORE IN FLUIDIZED BED**Nesibe ORT* and Sedat YÖRÜK****

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Abstract

In this study, direct reduction of Attepe iron ore in a laboratory type fluidized bed reactor by N_2 , CO, CO_2 , H_2 and H_2O containing gas mixtures of various compositions at 600, 700 and 800 °C was investigated. The results showed that the ore contained 9% (w/w) of bounded water and the structure was significantly altered during the pre-heating and reduction steps due to both dehydration and sintering. It was determined that reduction of Fe_2O_3 consisted of 2 stages. The rate of the first region including $Fe_2O_3 \rightarrow FeO$ conversion was commonly controlled by the nucleation of wustite in both reaction conditions convenient for wüstite or metallic iron formation. By the time all surface of the reacting particle was covered by dense wustite layer at reaction conditions where wustite was stable, further reduction was able to be accomplished only by solid-state diffusion and solid-state reaction of electrons and ferrous ions. In that instance second stage of the reduction including the exact conversion of Fe_2O_3 to FeO was solid-state reaction and solid state diffusion controlled. However, if the reaction conditions were convenient for the formation of metallic iron, the porous iron layer enabled to gas diffusion. Herewith the second stage of the reduction including the $FeO \rightarrow Fe$ conversion substantiated under the control of chemical reaction at FeO/Fe interface.

Keywords: Direct reduction, direct reduced iron, sponge iron, fluidized bed, gas-solid kinetics**1. Introduction**

Contemporarily, world crude steel production is achieved by two methods. In the first method, all production steps from raw materials like iron ore, coke and limestone to final product of crude steel are fulfilled in integrated plants consist of traditional BF (blast furnace) and BOF (basic oxygen furnace) units [1]. This method supplied 70% of the 2010 World crude steel production of 1414 Mtons according to WSA (World Steel Association) reports. In the second method, steel production is accomplished by smelting scrap with various proportions of DRI (direct reduced iron) in EAFs (electric arc furnace). The latter method supplied 10% of the World crude steel production in 1950s and enhanced its contribution to production within the years. In 2010, 28% of the World crude steel production was fulfilled by EAFs [2]. The increment in EAF steel production gives rise to difficulties on scrap recruitment in international marketing. Current state enhances the importance of the direct reduced iron (DRI) which can be evaluated as a qualified alternative to the scrap [3].

Other reasons make DRI a remarkable charge material for EAFs are, its clean chemical composition and efficient melting properties compared to scrap [4] and environmentally friendlier character of DR (direct reduction) processes. Furthermore, through the hot charging facility of DRI as HDRI (Hot Discharged Direct Reduced Iron), it is possible to reduce energy consumption in EAFs in proportion to cold scrap charging option.

Due to all above mentioned reasons, World total DRI production rose by approximately 85 percent from about 38 to 71,3 Mtons through the years 1999-2010. Thus the DR of iron ores turns into an issue of increasing importance in terms of Iron & Steel Industry [5].

In this study, direct reduction of Attepe iron ore by N₂, CO, CO₂, H₂ and H₂O containing gas mixtures of various compositions in a laboratory type fluidized bed reactor at 600, 700 and 800 °C was investigated.

2. Experimental

The experiments were carried out in a fluidized bed reactor made of quartz and endowed with a porous gas distributor disk of 20 mm in diameter. There was also a slot for the thermocouple, lying down throughout the vertical axis of the reactor and enables to follow the temperature of the reaction zone.

The iron ore, whose chemical and physical properties are given in Table-1 and Table-2, was supplied from Attepe-Turkey. In all reduction experiments, ore samples of 0,25-0,35 mm diameter range [(-45+60) mesh ASTM size fraction] were processed. The H₂, CO, CO₂ and N₂ gases used for reduction were of 99% purity and a humidifier unit was used in order to enrich the reducing gas with steam in cases it had to contain H₂O. The linear velocity of the synthetic reducing gas mixture was four times of the u_{mf} (minimum fluidization velocity, (m/s) given in Eq.(1)[6] where d_p : particle diameter (m), ρ_s : solid density (kg/m³), ρ_{gas} : gas mixture density (kg/m³), g : acceleration due to gravity (9.81 m/s²), μ_{gas} : kinematic viscosity of gas mixture (kg/m.s)

$$u_{mf} = \frac{dp^2 \cdot (\rho_s - \rho_{gas}) \cdot g}{1650 \cdot \mu_{gas}} \quad (\text{Re}_p < 20) \quad (1)$$

Following the linear gas velocity calculation, volumetric flow rate of the reducing gas mixture was determined by multiplying the linear velocity with the area of porous distributor disk. For the desired gas composition to be attained, the volumetric flow rate of each gas specie in the mixture were controlled and adjusted by flowmeters. For all experiments, in order to obtain similar bed characteristics, the 50% of gas mixture was N₂, and the rest was shared by CO, CO₂, H₂ and H₂O according to the reaction conditions.

Table 1. Chemical analysis of the Attepe iron ore in %(w/w)

Ore	Fe ^{tot}	Fe ₂ O ₃	SiO ₂	CaO	MgO	Al ₂ O ₃	LOI	Other
Attepe	52.40	74.86	5.96	0.80	0.43	0.85	9.13	6.47

LOI: Lost of Ignition

Other: Mn, S, K₂O, Na₂O, P, Zn,Cu, As, Pb and iron silicates affected by neither DR reactions nor chromatometric analysis

Table 2. Physical properties of Attepe iron ore

Property	Value
True density	3760 [kg/m ³]
Bulk density	3350 [kg/m ³]
Ore porosity	12.06 [%]
Spesifik surface area	19.21 [m ² /g]

Subsequent to loading with approximately 10 g of ore, the reactor was placed into the furnace which was heated to the reaction temperature. The reactor was purged with N₂ at fluidized conditions, until the central temperature displayed by the thermocouple reached to the desired value in order to prevent excessive sintering. When the aimed temperature was attained, the purging stream was switched to the reducing mixture so as to reduce the iron ore for a predetermined reaction time.

Following the reduction, the reactor was removed from the furnace, and the gas stream was changed back to N₂. Then the reduced iron ore samples were cooled down under N₂ atmosphere to the ambient temperature, transferred into glass bottles in an effort to prevent any contact with air and reoxidation and analysed by chromatometry [7,8] so as to determine the reduction degree given in Eq.(2).

$$\text{Degree of reduction} = \frac{\text{Amount of oxygen removed from ore by reducing gas}}{\text{Initial oxygen content of the ore}} \quad (2)$$

The reduction tests were performed for 2, 5, 10, 15, 20 and 40 minutes at 600, 700 and 800 °C reaction temperatures and reducing gas mixture compositions given in Table 3. Percentage of the each gas specie was chosen from the wustite-stable or Fe-stable region of the equilibrium gas composition diagrams of Fe-O-C and Fe-O-H systems given in Fig.1. [9].

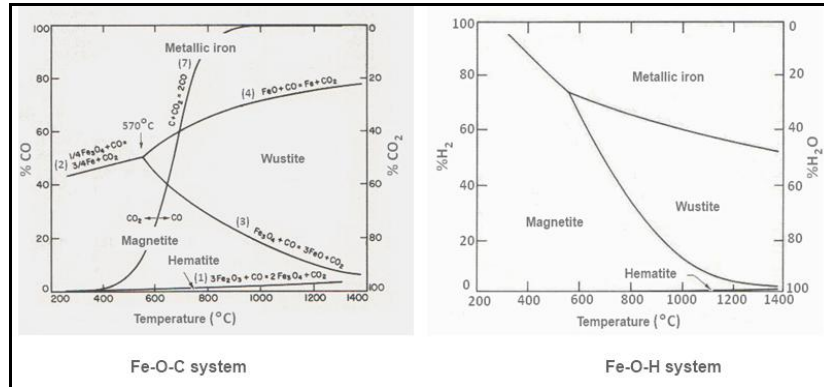


Figure 1. Fe-O-C and Fe-O-H equilibrium diagrams

Table 3. Reducing gas mixture compositions used in experiments % (v/v)

N ₂	CO	CO ₂	H ₂	H ₂ O	Stable phase
50	25	25	-	-	Wustite
50	35	15	-	-	Metallic iron
50	42	8	-	-	Metallic iron
50	-	-	35-25*	15-25 [#]	Wustite
50	-	-	40	10	Metallic iron
50	-	-	45	5	Metallic iron
50	20	5	20	5	Metallic iron
50	22	3	23	2	Metallic iron

* 35% at 600 °C, 30% at 700 °C and 25% at 800 °C

[#] 15% at 600 °C, 20% at 700 °C and 25% at 800 °C

3. Results and Discussion

As can be seen from the TG graph given in Fig. 2. (acquired by NETZSCH STA 409 PC/PG at 10 °C/min. heating rate and under 60 ml/min. N₂ stream), Attepe iron ore consists of 9% (^{w/w}) bounded water which leaves the structure between 250-400 °C range. The dehydration has a significant effect on pore structure which influences the reducibility of the ore since each reduction experiment is carried out afterwards a pre-heating treatment explained in the previous section.

Effects of dehydration and sintering on pore structure and reduction behaviour of the ore were investigated thoroughly in elsewhere before [10-12]. To sum up, reducibility of the ore is severely diminished right before the reduction due to the dehydration occurred during pre-heating under inert stream. In pursuit of switching the reducing gas, the effect of the sintering (stems from reaction temperature) stands out. Actually reaction temperature has twosided influence on reduction behaviour of ore; the increase on temperature both accelerates the reduction rate and enriches the equilibrium composition but at the same time causes sintering which inactivates reaction sites and decreases the reduction rate. It is determined that, sintering effect of the reduction temperature is dominant.

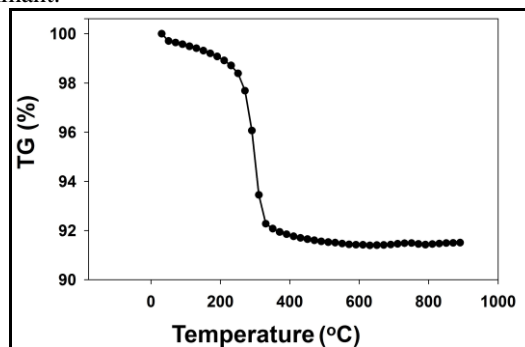


Figure 2. Thermal gravimetric decomposition graph of Attepe iron ore

A typical "t-Degree of reduction" graph obtained by (50% N₂+25% CO+25% CO₂) containing gas mixture at 600 °C is given in Fig.3.

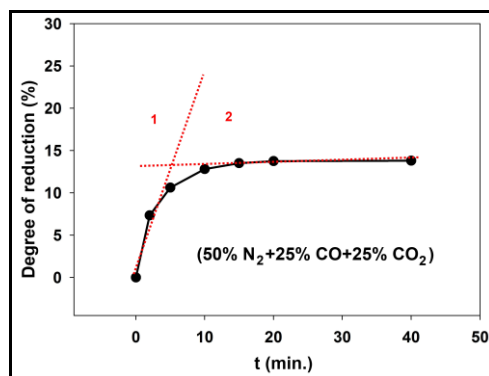


Figure 3. A typical "t-Degree of reduction" graph obtained at 600 °C

As can be seen from Fig.3., reduction rate of the ore significantly decreases after a speedy inception region and further reduction progresses with a notably lower rate (in reaction conditions which wustite is stable almost no further reduction occurs). All reduction degree curves obtained by Attepe iron ore follow same route with some differences on time and degree of reduction values depending on the reducing gas composition and reaction temperatures. The shoulder seen on "t-Degree of reduction" curves led to an idea that reduction mechanism and rate controlling step changed beginning from that point. Therefore the reduction curves divided into 2 regions in order to perform a more accurate kinetic analysis.

3.1. First Region

Gaseous reduction of hematite above 570 °C proceeds according to the sequence given in Eq.3.



In hematite the oxygen atoms are arranged in the closed-packed hexagonal structure but they form a face-centered cubic structure in magnetite and in wustite. Therefore in the first stage of reduction, i.e. $\text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4$ conversion, oxygen atoms undergo a severe readjustment which results in about a 25% increase in volume [9]. The porosity formed during the aforementioned swelling process provides wider reacting area for reducing gas and accelerates the reduction rate. Additionally, even a small amount of reductant concentration is sufficient to complete $\text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4$ conversion as seen on Fig.1 since the thermodynamic equilibrium composition at reaction conditions consists of almost entirely magnetite. These facts can be used to explain the speedy inception region on Fig.3.

For the following steps ($\text{Fe}_3\text{O}_4 \rightarrow \text{FeO} \rightarrow \text{Fe}$) there is a consensus on literature [9,13] that FeO has a dense structure which obstructs reducing gas access into FeO/Fe interface, even it has been formed by reduction of a porous hematite ore. Therefore this region is basically controlled by nucleation of wustite irrespective of the reaction conditions are thermodynamically convenient for wustite or metallic iron formation. Thus, Hancock-Sharp Equation was chosen for modelling of that region i.e. $\text{Fe}_2\text{O}_3 \rightarrow \text{FeO}$, and curves of higher linear regression coefficients (meanly 0,98) were obtained compared to other model equations. The model fitted well with the experimental data for all gas compositions and reductant species i.e. H_2 and/or CO. A typical Hancock-Sharp model graph obtained by (50% N_2 +25% CO+25% CO_2) containing gas mixture is given in Fig.4. so as to be an example.

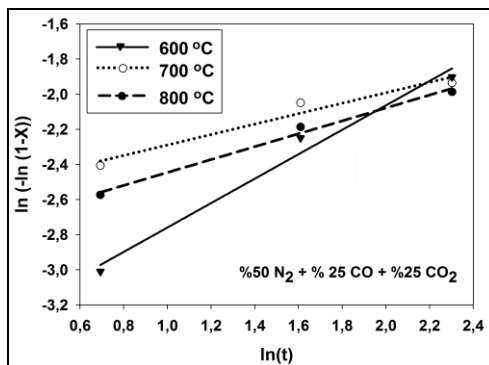


Figure 4. Hancock-Sharp model graph of $\text{Fe}_2\text{O}_3 \rightarrow \text{FeO}$ conversion carried out at (50% N_2 +25% CO+25% CO_2) reducing gas composition

3.2. Second Region

By the time nucleation of wustite completed and surface of the reacting particle is covered by a dense wustite layer, second region of the reduction path is arrived. In this region, the reduction mechanism follows 2 different routes according to the reaction conditions;

- If the thermodynamically stable phase determined by temperature and reducing gas composition is wustite, access of reducing gas into the unreacted inner parts of the particle is prevented by the dense wustite layer covering the particle surface. Hence, further reduction involving completion of $Fe_2O_3 \rightarrow FeO$ conversion is able to be accomplished only by solid-state diffusion and solid-state reaction of electrons and ferrous ions [14-16]. In this instance second stage of the reduction including the exact conversion of Fe_2O_3 to FeO is solid-state reaction and solid state diffusion controlled. After this point, the reduction advances with a negligibly low reaction rate so it is possible to say that no further reduction is achieved in practice (see Fig.3. region 2).

- However, if the reaction conditions are convenient for the formation of metallic iron, the porous iron layer –that is why DRI is mostly referred as "sponge iron"- enables the gas diffusion into the FeO/Fe interface. Herewith the second stage of the reduction including the $FeO \rightarrow Fe$ conversion substantiates under the control of chemical reaction at FeO/Fe interface. Mc. Kewan chemical reaction control model was chosen in order to represent the experimental data belong to the $FeO \rightarrow Fe$ conversion region of "t-Degree of reduction" curves for each reductant specie i.e. CO and/or H_2 . A typical Mc. Kewan chemical reaction control model graph obtained by (50% N_2 +35% CO+15% CO_2) containing gas mixture is given in Fig.5.

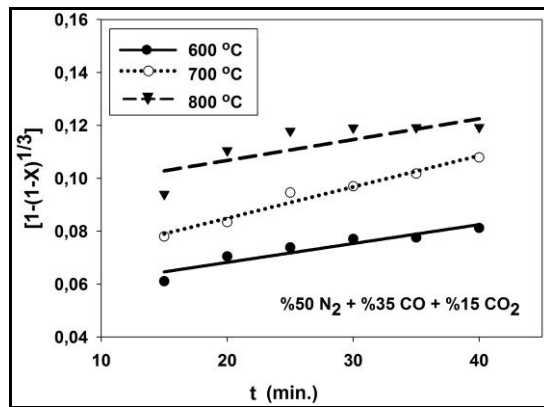


Figure 5. Mc. Kewan model graph of $FeO \rightarrow Fe$ conversion carried out at (50% N_2 +35% CO+15% CO_2) reducing gas composition

4. Conclusions

- Attepe iron ore consists of 9% (w/w) bounded water, whose dehydration causes radical changes on pore structure. Furthermore sintering arises from reaction temperature has a notable effect on reduction rate.
- Reduction of Fe_2O_3 consists of 2 stages as shown in Table 4.

Table 4. Stages and controlling mechanisms of gaseous reduction of Fe_2O_3

Thermodynamically stable phase determined by T and gas composition	1 st stage	Controlling mechanism for 1 st stage	2 nd stage	Controlling mechanism for 2 nd stage
Wustite	$Fe_2O_3 \rightarrow FeO$ conversion	Nucleation of wustite	Completion of $Fe_2O_3 \rightarrow FeO$ conversion	Solid state diffusion and solid state reactions.
Metallic iron	$Fe_2O_3 \rightarrow FeO$ conversion	Nucleation of wustite	$FeO \rightarrow Fe$ conversion	Gas-solid chemical reaction at FeO/Fe interface

- As seen on Table 4., the first stage of the hematite reduction is common for both 2 situations where the thermodynamically stable phase is wustite or metallic iron and can be represented by Hancock-Sharp nucleation model successfully.

- The route of the second region is determined by the final product. In case wustite is stable, further reduction is provided by solid state diffusion and reactions of electrons and ferrous ions which have negligibly slow rate. If metallic iron is stable, further reduction is implemented by gas-solid reaction takes place on FeO/Fe interface. In this case, Mc. Kewan chemical reaction control model can be used to represent the experimental data.

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