

The Effects of Volatile Materials of Non-coking Coal on the Reduction of Hematite

O. Ganji^{1*}, S. Raygan², J. Vahdati Khaki³

¹ Department of Materials Engineering, Islamic Azad University, Tehran South Branch, Tehran, Iran

² School of Metallurgy and Materials Engineering, University of Tehran, Tehran, Iran

³ Iron and Steel Research Center, Ferdowsi University of Mashhad, Mashhad, Iran

Abstract

One of the most important methods to produce sponge iron is coal based reduction of iron ore. Direct reduction methods based on coal are being improved due to the abundance of coal sources and its lower cost in comparison with natural gas. Volatile materials in coal play an important role in the reduction of iron oxides. In this study, noncoking coal with high volatile materials from Iran and commercial hematite with the purity of 98% were used to investigate the effect of volatile materials on the reduction process. The effects of reduction time (0 to 75 minutes), temperature of reduction (700 to 1000 °C), particle size of coal (53 to 250 micron), and the ratio of carbon content of coal to hematite (0.9 to 1.2) were investigated. The results indicated that volatile materials could reduce 56% of iron oxide. The XRD results of reduced materials implied the stepwise reduction process. Furthermore, activation energy was increased with increasing the degree of reduction.

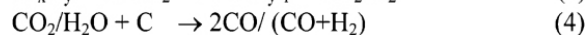
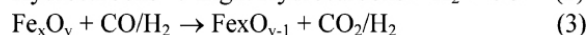
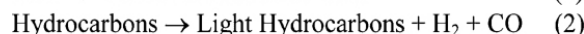
Keywords: Reduction of Hematite, Volatile Materials, Coal.

1. Introduction

The blast furnace process is still the predominant method for primary iron production. However, the disadvantages inherent in the process have led to the development of alternative processes such as the mini blast furnace, smelting reduction, and direct reduction processes. Many of these alternative processes are still under development. However, direct reduction processes have reached some level of commercial applicability and are considered to be the most developed alternative iron making route. It is coke-less and environmentally friendlier when compared to the blast furnace process ¹⁾.

Nowadays, there has been considerable interest in the reduction of iron oxides by solid carbon ²⁾. Direct reduction of iron ore/oxides by solid reductant has gained considerable importance for producing iron economically through alternative routes other than the conventional Blast Furnace process ³⁾. The biggest advantage of the DRI technologies relies on the fact that DRI does not require coke making and sintering processes ⁴⁾. It is generally agreed that the reduction of iron oxide by carbon occurs through the gaseous

intermediates CO and CO₂ ²⁾. The reaction sequence of reduction by volatile matter above 600 °C can be represented by equations 1 to 4 ⁵⁾:



The complexity of iron oxide reduction is increased when noncoking coal is used as a reductant because it contains a considerable amount of volatile materials. Below 350°C, most of the chemisorbed H₂O will evolve during the early stages of heating followed by the light gases of CO, H₂, CO₂, CH₄ and C₂H₆, which are developed in the range of 350 -600°C. Above 600°C, complex hydrocarbons or tars (MW_{Tar} ≥ 300 g/mole) consisting of large chains of carbon and hydrogen are released ⁵⁾. The released volatiles can be dissociated at high temperatures to generate highly reducing gases like CO and H₂. There is not enough knowledge about the nature and extent of the reaction between iron-oxide and these volatiles. This paper tries to determine the effect of reduction parameters such as reduction temperature, particle size of the coal and C/Fe₂O₃ molar ratios on the reduction behavior of hematite powder by volatile materials evolved from non-coking coal.

2. Experimental Procedure

In this study, commercial hematite with the purity of 98% and noncoking coal with high volatility

* Corresponding author:

Tel: +98 915 3034907

Fax: +98 511 6024360

Email: omid_forging@hotmail.com

Address: Department of Materials Engineering, Islamic Azad University, Tehran South Branch, Tehran, Iran

1. M.Sc Student

2. Associate Professor

3. Professor

were used. Results of proximate analysis of Gol-Bano noncoking coal, based on the ASTM standard methods (D3173, D3174, and D3175) and chemical composition of hematite by XRF, are indicated in tables 1 and 2, respectively.

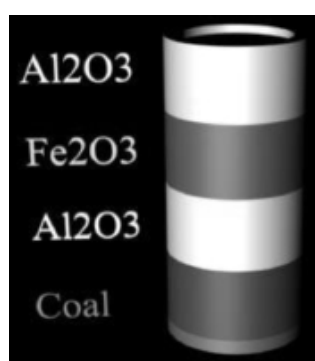
Table 1. Proximate analysis of Gol-Bano noncoking coal.

Composition	Fixed carbon	Ash	Moisture	Volatiles
Wt%	50	8	4	38

Table 2. Chemical composition of hematite.

Composition	Fe ₂ O ₃	Cl	CaO	MnO	SiO ₂	SO ₃
Wt%	97.930	0.976	0.426	0.309	0.140	0.075

The other used material in these experiments was commercial alumina as an inert layer. The materials were set in the main crucible in four layers without any compression (Figure 1).



(a)



(b)

Fig. 1. Schematic of the materials layers in crucibles, (a) the main crucible, (b) the testifier crucible.

The first layer from the bottom of the crucible was coal (5gr). The second, third and fourth layers were alumina (10gr), hematite (10gr) and alumina

(5gr), respectively. The main goals of setting an inert alumina layer between two layers of coal and hematite were preventing mixing of hematite and coal and decreasing the emersion rate of volatile materials. The fourth inert alumina layer prevented volatile materials evolved from the crucible and oxidation of reduction products. The second crucible as the testifier consisted of layers of coal and alumina (Figure 2).

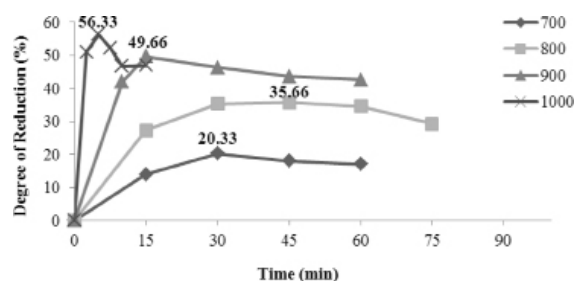


Fig. 2. The effect of temperature on the reduction of hematite by coal with C/Fe₂O₃ molar ratio of 1.1, particle size of coal: ≤ 53 micron.

In order to make the same condition in the two crucibles and also, simulate the evolution of volatile materials not taking part in reaction, the height of materials in the main and testifier crucibles were considered equivalent. The degree of reduction was calculated according to equation 5. In this equation, W_{O₂} and ΔW_{Fe₂O₃} stand for the total weight of oxygen in hematite and the loss of weight of hematite, respectively.

$$R = \frac{\Delta W_{(Fe_2O_3)}}{W_{(O_2)}} \times 100 \quad (5)$$

3. Results and Discussion

3.1. The effect of Time and Temperature on the Reduction Process

Figure 2 indicates the effect of temperature on the reduction degree of hematite and coal with the particle size being below 53 micron. The particle size of alumina and the molar ratio of C/Fe₂O₃ were 44 micron and 1.1, respectively. It was seen that at constant reduction time, increasing temperature caused the increase in the weight loss of hematite and the degree of reduction. This was in agreement with other reports^{3,6-10}. It was observed that the rate of reaction was increased exponentially with temperature.

Figure 2 also shows that at the early stage of reduction, the rate of reduction in the hematite layer was increased with temperature as a consequence of faster evolution of volatiles. It seems that after maximum reduction value, the pressure of evolved volatile materials was decreased and the oxygen of air which oxidized the reduced products entered the crucible. Thus, the reduction degree was dropped gradually.

The XRD analysis of reduced oxide at 700, 800 and 1000 °C, in comparison with hematite, has been shown in Figure 3.

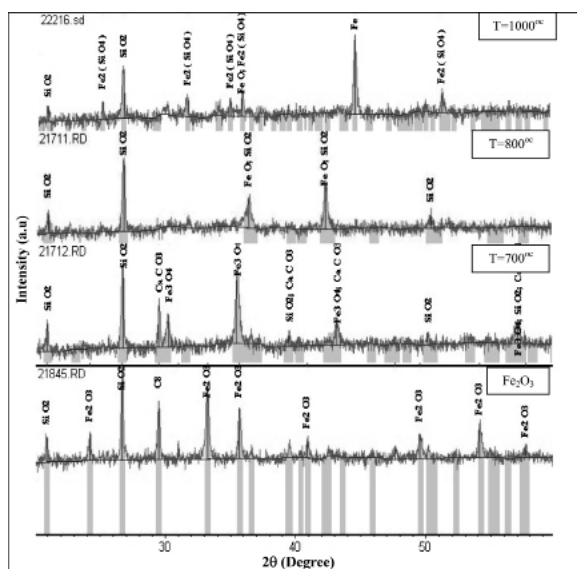


Fig. 3. XRD patterns of the hematite & reduction products at 700, 800 and 1000°C.

This Fig implies the stepwise reduction process of hematite reduction according to the following steps:



These observations are in agreement with the results of other researchers^{4,7,8,10}. According to stepwise direct reduction, the degree of reduction of Fe_2O_3 is: 11.11%, 33.33% and 100% for Fe_2O_3 to Fe_3O_4 , Fe_3O_4 to FeO and FeO to metallic Fe , respectively. The results in Fig. 1 and related XRD patterns have proved that the degree of reduction in 700°C is more than that of Fe_2O_3 to Fe_3O_4 stage. Therefore, the reduction has passed through this step. The step of reduction in Fe_3O_4 to FeO has been completed above 750°C. XRD patterns imply that about 800°C reduction of FeO to metallic Fe has occurred.

3.2. The effect of Particle Size of Coal on Reduction

Figure 4 shows the effect of particle size of coal on the reduction degree of hematite at the temperature of 1000 °C.

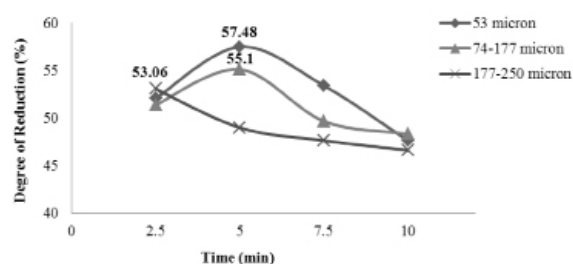


Fig. 4. The effect of coal particle size on the reduction of hematite with $\text{C}/\text{Fe}_2\text{O}_3$ molar ratio of 1.1 at 1000°C.

Figure 4 demonstrates that the degree of reduction was increased with decreasing coal's particle size. The free surface area of small particles was more than that of large particles. Therefore, the amount and rate of evolved volatile gases in small particles of coal were more in the early stages of reduction. Moreover, the rate of diffusion of gases toward the outside of the crucible was slower in layers consisting of small particles. As a consequence, the degree of reduction was increased with decreasing the particle size of coal.

It can be observed that the maximum degree of reduction was reached in fewer times for larger particles size. The reason for this phenomenon is variation in the chemical composition of removing volatile materials with increasing the particle size because increasing the particle size accelerates the second reactions of producing methane and carbon oxides²). Thus, the maximum degree of reduction can be reached in fewer times. According to the results, the maximum degree of reduction for various particle sizes takes place in 5 minutes except for (177-250) micron.

3.3. The effect of $\text{C}/\text{Fe}_2\text{O}_3$ Molar Ratio on Reduction

The effect of $\text{C}/\text{Fe}_2\text{O}_3$ molar ratio on the degree of reduction of hematite after 15 minute reduction at the temperature of 900 °C can be observed in Figure 5.

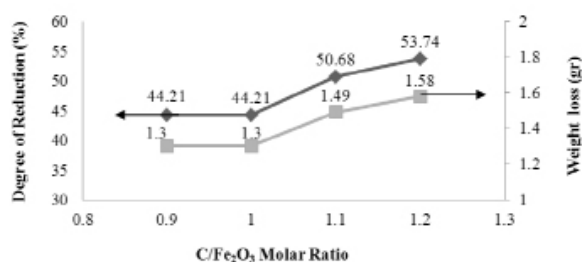


Fig. 5. The effect of carbon content/hematite on the reduction at 900 °C, 15 min.

It can be observed that the degree of reduction and weight loss of hematite layer was improved with increasing the weight ratio of carbon of the coal to hematite. The amount of volatile materials was increased with this molar ratio, resulting in an increase in the evolved gases and subsequently, the degree of the reduction. The evolution rate of volatile materials could also be increased, causing more reduction.

3.4. Evaluating the activation energy of reduction

Activation energy value can be calculated by integration method according to Figure 6¹¹⁻¹³.

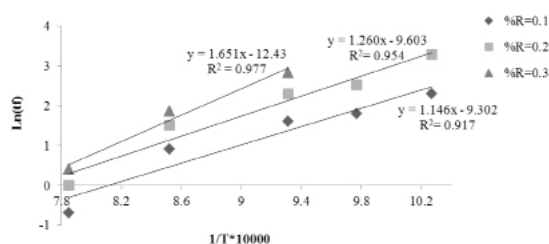


Fig. 6. Plot of $\ln(t_f)$ vs. $10^4/T$ for the reduction of hematite with C/Fe_2O_3 molar ratio of 1.1.

In this method, the times related to the constant degree of reductions in various temperatures can be obtained from equation 7:

$$t_f = \frac{\text{Constant} \cdot \exp\left(\frac{E}{RT}\right)}{A} \quad (7)$$

where K is the constant of the rate of reaction, A is factor of frequency, E is activation energy, R is the constant of gases, T is temperature and t_f is the time required to reach the identified degree of reduction. Activation energy can be evaluated from the slopes of the linear curves in Figure 6 for the constant degree of reduction. The calculated activation energies in various degrees of reduction are summarized in Table 3.

Table 3. Activation energy for different degrees of reduction.

Degree of Reduction, (%)	10	20	30
Activation energy (kJ/mol)	95.27	104.75	137.26

The results indicated that activation energy was increased with increasing the degree of reduction.

Results in Table 3 indicate that activation energy was increased with increasing the degree of reduction.

Both removed volatile materials and mass transfer were increased with increasing activation energy. According to the degrees of reduction that make it possible to evaluate activation energy and the numbers, in the lower degree of reduction, exhausting of volatiles was easier and faster; thus activation energy was lower too. At higher degree of reduction, on the one hand, exhausting of volatiles and cracking of complex hydrocarbons were more difficult; on the other hand, removed volatiles rate was decreased and mass transfer was harder; thus activation energy was higher.

4. Conclusions

According to the results of this study, the following conclusions could be drawn:

1. The degree of reduction was increased with raising the temperature because the rate and amount of volatile materials were increased, resulting in the fast removal of oxygen from hematite.
2. The maximum degree of reduction was increased with decreasing the particle size of coal due to increasing the amount of volatile materials. At long time, because of the aggregation of volatiles at the bottom of layers consisting of smaller particles, the reduction degree could be increased.
3. Raising C/Fe_2O_3 molar ratio resulted in an improvement in the degree of reduction due to increasing volatile materials and reductant gases.
4. In the lower degrees of reduction, exhausting of volatiles was easier and fast; thus, activation energy was lower. In the high degrees of reduction, on the one hand, exhausting of volatiles and cracking of complex hydrocarbons were more difficult; on the other hand, the rate of removed volatiles was decreased, mass transfer was harder, and the activation energy was higher.

References

- [1] B. Anameric, S. K. Kawatra: Miner. Process. Extr. Metal. Rev., 28(2007), 59.
- [2] R. J. Fruehan: Metall. Mat. Trans. B., 8(1977), 279.
- [3] S.K. Dey, B. Jana, A. Basumallick: ISIJ Int., 33(1933), 735.
- [4] G-S. Liu, V. Strezov, J. A. Lucas, L. J. Wibberley: Thermochim. Acta, 410(2004), 133.
- [5] I. Sohn, R. J. Fruehan: Metall. Mat. Trans. B., 36(2005), 605.
- [6] Y. K. Rao: Metall. Mat. Trans., 2(1971), 1439.
- [7] C. E. Seaton, J. Foster, J. Velasco: ISIJ Int., 23(1983), 490.
- [8] E. Kasai, T. Kitajima, T. Kawaguchi: ISIJ Int., 40(2000), 842.
- [9] G. M. Chowdhury, G. G. Roy, S. K. Roy: Mat. Trans. B., 39(2008), 160.
- [10] S. Halder, R. J. Fruehan: Mat. Trans. B., 39(2008), 796.
- [11] S. K. Dey, B. Jana, A. Basumallick: ISIJ Int., 33(1933), 735.
- [12] S. B. Sarkar, H. S. Ray, I. Chatterjee: J. Therm. Anal. Calor., 35(1989), 2461.
- [13] M. Kumar, P. Mohapatra, S. K. Patel: Miner. Process. Extr. Metal. Rev., 30(2009), 372.