Study on the reducibility of iron ore pellets at high temperature

Cao-Son Nguyen, Thanh-Hoan Nguyen, Son-Lam Nguyen, Anh-Hoa Bui*

School of Materials Science and Engineering, Hanoi University of Science and Technology

Abstract:

The behaviour of iron ore pellets in a blast furnace must be considered to improve ironmaking operations, especially when a large amount of the pellets is used. This study presents the reduction degree, mineralogical composition, and morphology of the pellet reduced in a gas mixture of 60% CO and 40% Ar at temperatures between 900 and 1,100^{o}C. The pellet was prepared from iron ore from the Cao Bang province, Vietnam, by rotary drum. The obtained results showed that the reduction degree of the pellet increased with increasing reduction time and temperature. The activation energy of the reducing reaction was calculated to be 63.2 kJ/mol, which indicated that reduction occurred more easily in the present condition. X-ray diffraction (XRD) results revealed mineralogical phases such as hematite (Fe_2O_3), magnetite (Fe_3O_4), wüstite (FeO), metallic iron (Fe), and fayalite (Fe_2SiO_4) existing in the pellets when reduced for different times and temperatures. Fe and Fe_2SiO_4 were found to be the majority in the pellet that was reduced for 90 min at 1,100^{o}C. Scanning electron microscopy (SEM) observations suggested the formation of a liquid phase, e.g., Fe_2SiO_4, which retarded the reducing reaction because it hindered the diffusion of gas flow inside the pellet. This phenomenon is essential to blast furnace ironmaking because pellets must be completely reduced before they move down to the liquid zone.

Keywords: **blast furnace, iron ore pellet, mineralogy, morphology, reduction degree.**

Classification numbers: **2.1, 2.3**

Introduction

Because fine iron ore cannot be used in a blast furnace, sintering or pelleting processes need to be applied to make lump ore. Among those methods, pelleting is considered to be superior to sintering in the aspect of environmental performance [1]. The rich and fine (smaller than 40 μm grain size) iron ores cannot be used for sintering, however they are efficient for fabricating pellets [2]. As a raw material, iron ore pellets have contributed to the improvement of operating efficiencies and stability during ironmaking in a blast furnace [3-5]. Therefore, it is important to increase the ratio of pellets used in the furnace for both improved environmental friendliness and to promote the healthy operation of blast furnace ironmaking.

The behaviour of the pellet in a blast furnace at high temperature has been of great interest to those wanting to increase the amount of pellets in a blast furnace. However, increasing the pellet ratio faces some challenges due to the formation of a liquid phase in the pellet at increased temperature [6, 7]. The temperature of the pellet increases when they move down to the lower part of the blast furnace and make contact with the high temperature gas ascending from the tuyeres. The appearance of a liquid phase would have a negative effect on the reducibility of the pellets due to the prevention of reduction gas flowing into the pellet. It has been acknowledged that the reducibility of the pellet is an important factor for the evaluation of pellet utilization in a blast furnace. In turn, the reducibility is largely influenced by changing pellet morphology at high temperature. Despite the fact that there are some research works focusing on this issue, there is a lack of information on the morphology and reduction kinetics of the Vietnamese pellet at high temperatures. This study investigates the reduction kinetics and morphology of the pellet, which was made of iron ore from the Cao Bang province of Vietnam. Also, the mineralogical composition of the pellet in the reduced atmosphere was clarified and discussed.

Corresponding author: Email: hoa.buianh@hust.edu.vn

Experimental method

Iron ore was taken from the Cao Bang province of Vietnam. Iron ores and bentonite powders, which both had grain sizes below 25 µm, were completely mixed in a rotating machine for 10 min. The ratio of bentonite and iron ore was 2:98 in mass. The chemical and mineralogical compositions of the iron ore and the bentonite were analysed and is given in Table 1.

Table 1. The compositions of the used iron ore and bentonite (% mass).

The iron ore				
Fe_3O_4	Fe_2O_3	SiO_2	$Fe_2O_3.H_2O$	$CaCO_3+CaSO_4.2H_2O$
59.53	21.05	8.36	7.76	3.30

The bentonite							
Al_2O_3	CaO	Fe_2O_3	MgO	SiO_2	TiO_2	Na_2O_3	LOI
14.13	1.84	13.29	2.15	55.59	2.00	2.85	8.15

Green pellets were prepared from the ore using a rotary drum, as shown in Fig. 1. When the mixture was charged into the rotary drum, some small pellets were initially formed. The mixture was continuously added together with sprayed water, which caused the formed pellets to gradually grow. The total moisture content was controlled to be about 10% of the mass of the mixture during the pelleting process. Finally, green pellets were obtained with suitable grain size varied from 10 to 16 mm. For the purpose of increasing strength, the green pellets were heated at 1,200°C in a resistance furnace for 120 min and then cooled down to room temperature together with the furnace.
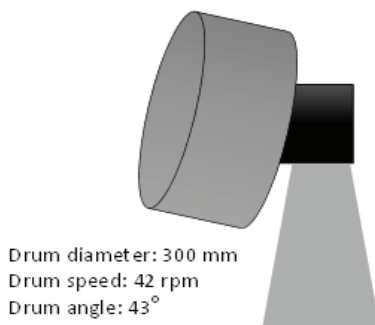

Drum diameter: 300 mm
Drum speed: 42 rpm
Drum angle: 43°

Fig. 1. Rotary drum machine.

Reducibility of the pellet was examined in the system shown in Fig. 2. The reduction gas (60% CO + 40% Ar) was controlled at a flow rate of 80 ml/s and introduced into a vertical alumina tube of the resistant furnace. The pellet was put inside a crucible that was connected with a balance on the top of the system. The weight of the pellet was lost due to oxygen removal from iron oxides during the reduction process so the reduction degree (f) was calculated using Eq. 1:

$$f = \frac{m_0 - m_t}{m_0} \times 100 \qquad (1)$$

where m_0 and m_t are the weight of the pellet before and after the reduction, respectively.
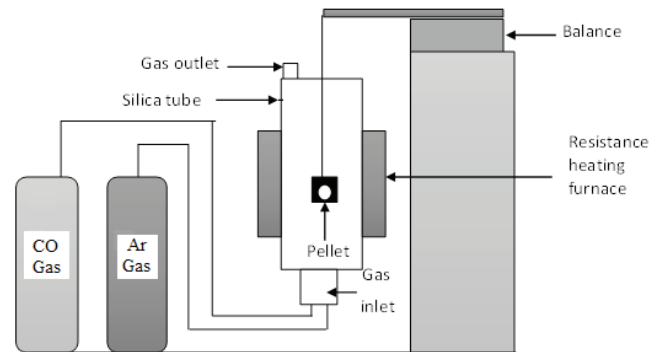

Fig. 2. Schematic diagram of the experimental setup for reducibility test.

The reduction degree of the heated pellets was examined at 900, 1,000, and 1,100°C. After cooling in the furnace, the mineralogical characteristics of the pellet were investigated using X-ray diffraction (XRD, Bruker) and the microstructure was observed using a scanning electron microscope (SEM, Jeol).

Results and discussion

Reduction process of pellets at high temperature

Fig. 3 shows the XRD pattern of the pellets reduced at different reaction times. The peaks of magnetite (Fe_3O_4) and wüstite (FeO) were observed in the pellet after 20 min, i.e., an indirect reduction of hematite (Fe_2O_3) to Fe_3O_4 was confirmed following reaction 1. When the pellet was reduced for 30 min, the peak of Fe_3O_4 significantly weakened and FeO was observed as shown in Fig. 3B. It was confirmed that FeO was obtained due to the partial reduction of Fe_3O_4 in accordance with reaction 2. Careful examination of XRD results showed that there was fayalite (Fe_2SiO_4 or $2FeO.SiO_2$) existing in the pellet. This is attributed to the contact of SiO_2 and reduced FeO, which then resulted in the formation of Fe_2SiO_4 (reaction 3). In addition, the reduction of Fe_2O_3 was found to

increase with reduction time. No peak from Fe_3O_4 was observed in the pellets that were reduced for 40 or 60 min (see Figs. 3C and 3D), but the peaks of FeO and metallic iron (Fe) were obtained with high intensity. When the reduction time was 90 min, the Fe peak strengthened and those of Fe_2SiO_4 weakened significantly (Fig. 3E). The intensities of the FeO and Fe peaks increased as the pellets were kept longer in the reduced atmosphere and the reduction of FeO was present after 60 min reduction time at 1,100°C. This result has proved the transformation of Fe_2O_3 to FeO, which subsequently was reduced to Fe in reaction 4.
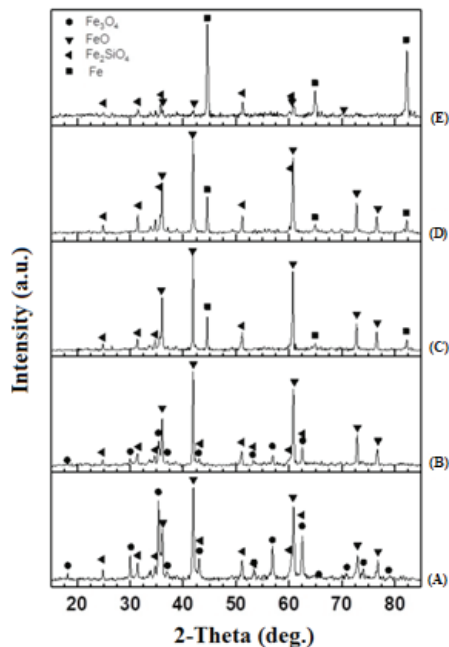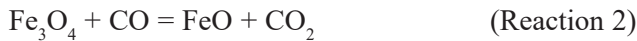
$$3Fe_2O_3 + CO = 2Fe_3O_4 + CO_2 \qquad \text{(Reaction 1)}$$

$$Fe_3O_4 + CO = FeO + CO_2 \qquad \text{(Reaction 2)}$$

$$2FeO + SiO_2 = Fe_2SiO_4 \qquad \text{(Reaction 3)}$$

$$FeO + CO = Fe + CO_2 \qquad \text{(Reaction 4)}$$

Fig. 3. XRD pattern of the pellets reduced at 1,100°C for (A) 20 min, (B) 30 min, (C) 40 min, (D) 60 min, and (E) 90 min.

Reduction kinetic of the pellet

Figure 4 shows an increase of the reduction degree with increasing reduction temperature. The reduction degree reached 89% at a temperature of 1,100°C after a reduction time of 90 min. Meanwhile, it was 80% for the case of 900°C after the same reduction time. This result is in agreement with the research of H. Chen, et al. (2015) [8].
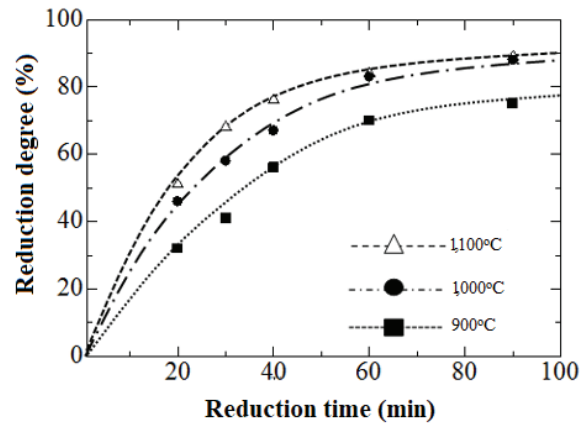

Fig. 4. Variation of the reduction degree with reduction time and temperature.

In order to correctly understand the reducibility of the pellet at high temperatures, the activation energy (E_a) was estimated. In this study, the values of the E_a (kJ/mol) were calculated using the Arrhenius equation:

$$\ln K = \ln A - \frac{E_a}{RT} \qquad (2)$$

where A is the Arrhenius factor or the frequency factor, K is kinetics constant, R ($JK^{-1}mol^{-1}$) is gas constant, and T (K) is temperature. The value of the constant K was calculated from the diffusion model of R. Zhong, et al. (2020) who proposed the reduction through a layer as in the following [9, 10]:

$$Kt = [1 - (1-f)^{1/3}]^2 \qquad (3)$$

where f is the reduction degree, K is coefficient constant, and t (min) is time. From the reduction results, a linear relationship between $[1-(1-f)^{1/3}]^2$ and time was plotted in Fig. 5, which shows the calculated K values as the slope of the straight line.
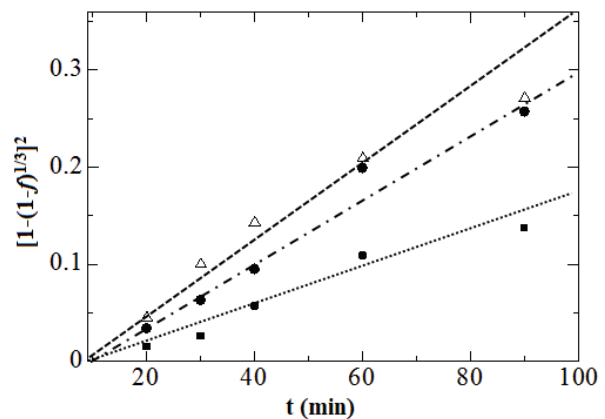

Fig. 5. Relationship between $[1-(1-f)^{1/3}]^2$ and time.

After calculation of the K value, the relationship between ln$K$ and $(1/T)$ was plotted in Fig. 6, where the value of E_a was calculated from the slope of the straight line. The calculated E_a was about 63.2 kJ/mol for the reduction of the iron ore in the present condition. It is known that the initial reactant could be Fe_2O_3 or Fe_3O_4 in the reduction process of iron oxides. According to S.P. Trushenski, et al. (1974) and W.K. Jozwiak, et al. (2007) [11, 12], the values of E_a were reported as 118 and 115 kJ/mol for Fe_2O_3 and Fe_3O_4, respectively. The fact that E_a in this study is smaller than expected from the literature indicates that the reduction reaction of Cao Bang iron ore occurs more easily under the conditions of using 60% CO and a high temperature of 1,100°C.
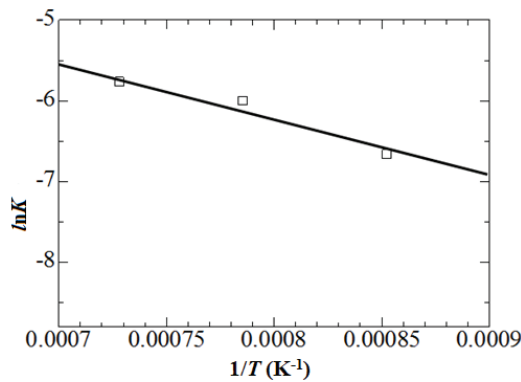

Fig. 6. Arrhenius plot for the reduction of the pellets.

Morphology variation with time affecting the reduction of the pellet

Figure 6 shows that the reduction degree significantly increased in the first 40 min of reduction time and remained slowly increasing until the end. The formation of the fayalite liquid phase would be the main factor diminishing the reducibility of the pellets. Clear evidence for this is given in Fig. 7, in which a liquid phase was seen in the pellet reduced for more than 20 min (Figs. 7B and 7C).
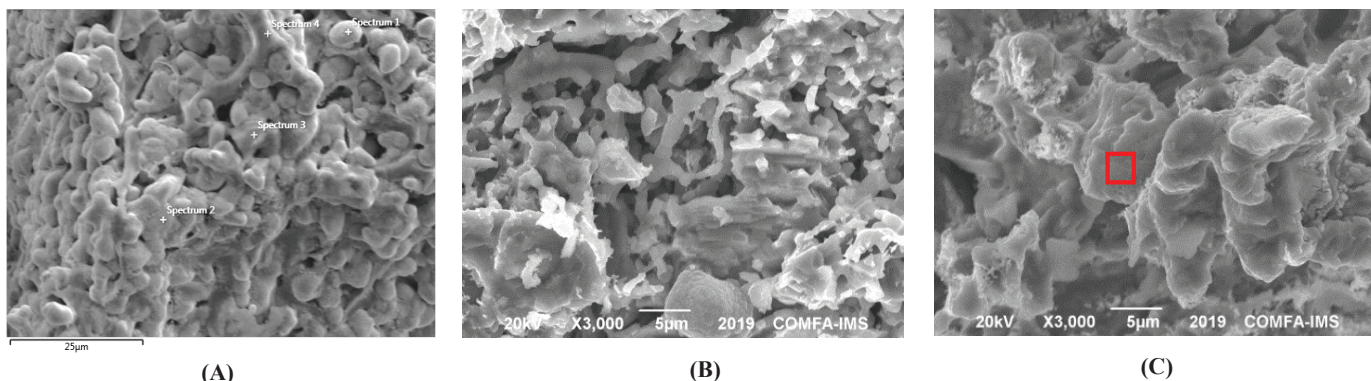
Table 2 shows the typical compositions of the liquid phase in the 40-min-reduced pellet using EDS analysis. The results suggested that the liquid phase contained fayalite (Fe_2SiO_4), which had a negative effect on the reducibility of the pellet. When the liquid phase occurs, it connects and creates larger liquid clusters, which were seen as the large blocks in the cooled pellets (Fig. 7C). The amount of the liquid phase in the pellet with 40 min reduction time was confirmed to be much more than that of the 20 min reduction. This finding was consistent with the results of L.Y. Yi, et al. (2015) [13] who concluded that the amount of liquid phase increased with increasing time at high temperatures and retarded the reduction rate of the iron oxide. Increasing the reduction time caused an increase of the liquid phase, which filled the pores of the pellet and finally shrank after the pellet cooled. The pores in the pellet are preferential for diffusion of the reduction gas, so the reduction degree must decreased with the porosity of the pellet [14]. This is similar to the other results, that is, that slag formation like fayalite retarded diffusion of the reducing gas flow within the pellet through the liquid layer and lead to a decrease in the reducibility of the pellet [15]. Therefore, it can be concluded that formation of a liquid phase is one of the main factors that decrease the reducibility of the pellet in a reduced atmosphere. This phenomenon plays a very important role in the operation of the blast furnace in which the pellets must be completely reduced before they move down to the liquid zone.

Table 2. The compositions of the liquid phase in the 40 min reduction (% mass).

O	Fe	Si	Al	Ca	Others
53.94	32.16	7.70	3.61	1.26	1.33

Fig. 7. SEM images of the pellets reduced at 1100°C for (A) 0 min; (B) 20 min; (C) 40 min.

Conclusions

The reduction degree, activation energy, and morphology of the pellets prepared from iron oxide of the Cao Bang province, Vietnam have been investigated in a gas mixture of 60% CO and 40% Ar at temperatures between 900-1,100°C. The main results are as follows:

1. The mineralogical composition of the pellet was identified by XRD, which validated the sequence of the reduction reactions proposed by the theory. Metallic Fe was confirmed to be prominent in the pellet reduced for 90 min.

2. A reduction degree of 90% after 40 min reduction time at 1,100°C was calculated based on the loss of pellet weight during the reduction. The reducibility of the pellet was found to increase with increased temperature.

3. The value of activation energy was calculated to be 63.2 kJ/mol for the reduced reaction of the Cao Bang iron ore. Reducibility was considered to be good in condition with a reduced atmosphere containing 60% CO gas and high temperatures.

4. SEM images of the pellets showed evidence of liquid formation - one of the main factors that decrease the reducibility of the pellet in the reduced atmosphere at high temperature. The amount of the liquid phase that negatively affected the reduction degree was confirmed to increase with increasing reduction time at 1,100°C.

COMPETING INTERESTS

The authors declare that there is no conflict of interest regarding the publication of this article.

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