

Thermogravimetric study of coal-based reduction of oolitic iron ore: Kinetics and mechanisms



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ABSTRACT

Oolitic iron ore is a refractory mineral resource of great importance due to its vast abundance in light of the dwindling supply of high quality iron ores globally. In this study, an oolitic iron ore was isothermally reduced by coal at 1423 K–1573 K, and the reduction kinetics and mechanisms were investigated using the thermogravimetry (TG) technique. The characteristics of reduced samples were analyzed by scanning electron microscope (SEM), energy dispersive spectrometer (EDS) and X-ray diffraction (XRD). It was found that the reduction temperature and C/O molar ratio had significant influence on the degree of iron oxide reduction and its reduction rate, and the coal-based reduction could be divided into the initial, middle, and final stages. The reaction kinetic models were proposed to represent the reduction of oolitic iron ore using coal. The hematite in the ore was reduced to metallic iron in the sequence of $\text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4 \rightarrow \text{FeO}$ (FeAl_2O_4 , Fe_2SiO_4) \rightarrow Fe. The mechanisms of reduction changed with reduction time. As reduction progressed, the oolitic structure was gradually destroyed, and the metallic iron aggregated concurrently. The rate controlling mechanisms during oolitic iron ore reduction were a combination of interfacial chemical reaction and solid state diffusion.

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1. Introduction

The persistently strong global demand for iron and steel has necessitated the utilization of various refractory iron ores, which are not suitable for direct blast furnace processes due to its low grades. In addition, the refractory iron ores cannot be upgraded cost-effectively using the traditional mineral processing methods because of its ultrafine grains and complicated mineral compositions (Sun et al., 2013a,b; Gao et al., 2013; Dang et al., 2013; Liu et al., 2012; Yu et al., 2013). Oolitic iron ore is such a refractory mineral resource of great importance due to its vast abundance globally in France, U.S., Canada, Egypt, the former Soviet Union, China, Pakistan, Italy and Saudi Arabia (Song et al., 2013; Zimmels et al., 1988; Abro et al., 2011; Adedeji and Sale, 1984; Manieh, 1984). Oolitic iron ores consist of ooids with concentric layers of alternate iron minerals and gangue minerals (Song et al., 2013; Zimmels et al., 1988). Oolitic iron ores have not been commercially exploited mainly because of the significant difficulties in the mineral beneficiation processes.

One promising approach to the utilization of oolitic iron ore is the direct reduction of iron oxides into metallic iron, followed by magnetic separation to recover metallic iron (Sun et al., 2013b; Srivastava and Kawatra, 2009; Li et al., 2011a,b). In particular, many efforts have been made to study oolitic iron ore reduction using coal as the reducing

agent. For instance, Li et al. (2011a), Sun et al. (2013b), and Li et al. (2011b) investigated the effects of reduction conditions on the metallization degree and iron recovery. The distribution behaviors of phosphorus and phosphorus removal during the coal-based reduction were examined by Sun et al. (2014a), Yu et al. (2013), Li et al. (2013a) and Li et al. (2014). The reaction behaviors of iron minerals and growth of metallic iron particles by coal reduction were assessed by Sun et al. (2013a). Han et al. (2014) further evaluated the effect of reduction conditions on the size distribution behaviors of metallic iron particles in reduced products. The aforementioned studies have demonstrated that high-grade metallic iron products (suitable for direct application in steelmaking) can be obtained from oolitic iron ores via coal-based reduction processes. However, most of these studies only examined the input materials and output products of the reduction processes. In our previous research, chemical analysis method was used to determine the degree of coal-based reduction of oolitic iron ore, and the kinetic models and mechanisms were tentatively proposed based on regression methods with four Avrami–Erofeev equations (Sun et al., 2014b). However, unlike thermogravimetry (TG) technique, the data obtained by chemical analyses were indirect with a long time interval (1 min) rather than real-time monitoring, and it was impossible to collect the data just from the one sample. Consequently, the observations may not accurately reveal the kinetics and mechanisms of coal-based reduction of oolitic iron ore, and further detailed research was warranted.

On the other hand, extensive research has been conducted in the reduction kinetics of iron oxides. For instance, El-Geassy (1996a), Kim

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et al. (2013), Hou et al. (2012) and Piotrowski et al. (2005) intensively studied the reduction kinetics of iron oxides by reducing gases such as CO, H₂, H₂-H₂O and CO-H₂ mixtures. The influence of different additives (CaO, MgO, SiO₂, Al₂O₃, MnO, NiO, Cr₂O₃) on the reduction of Fe₂O₃ was investigated in details by El-Geassy et al. (2008), Nasr et al. (1995), Khedr (2000), El-Geassy (1996b) and Hessein et al. (2008). The reduction kinetics of iron oxides by carbon (i.e., charcoal, coal and coke) was also reported by many researchers. For example, El-Geassy et al. (2013) analyzed the isothermal reduction kinetics of Fe₂O₃ and charcoal compacts by thermogravimetry (TG) and quadruple mass spectrometer (QMS) techniques. Strezov et al. (2005) and Liu et al. (2004) also examined the direct reduction of iron ore with coal using advanced experimental techniques (i.e., computational calorimetric method). Sun and Lu (1999) further proposed a non-isothermal and non-isobaric mathematical model to represent the reacting system of ore/coal composites. These research endeavors have imparted excellent insights into the reaction kinetics and mechanisms of iron oxides by reducing gases and carbon. However, the iron oxides used in these literatures were either high purity Fe₂O₃ or high grade iron ore (such as iron ore concentrate) that can be used directly in iron-making processes. Therefore, the kinetics and mechanisms presented by previous studies may not be suitable to the coal-based reduction of refractory iron ores, in particular, the oolitic iron ores.

The objective of the present study was to investigate the reduction kinetics and mechanisms of oolitic iron ore with coal as a reducing agent. The oolitic iron ore was isothermally reduced at different C/O molar ratios under different reduction temperatures with coal as the carbon source. The thermogravimetry (TG) technique was applied to measure the degree of reduction and reduction rate. Five structural models were used to describe the experimental data. The apparent activation energy, pre-exponential factor, and most probable mechanism functions were evaluated. The mechanisms of reduction process were revealed by SEM-EDS and XRD analyses.

2. Materials and methods

2.1. Materials

The oolitic iron ore used in this study was collected from the Guandian Iron Mine, Hubei Province, China. The results of chemical analysis and X-ray diffraction (XRD) analysis of the iron ore sample are shown in Table 1 and Fig. 1, respectively. The contents of total Fe, SiO₂, Al₂O₃ and CaO were 42.21%, 21.80%, 5.47% and 4.33%, respectively. The iron in the ore existed mainly as hematite (Fe₂O₃). The silicon and aluminum were distributed primarily in quartz (SiO₂) and chamosite ((Fe,Mg)₅Al₂Si₃O₁₀(OH)₈). In order to minimize the influence of the volatile matter on the reduction reactions, a low-volatile coal was used as a reducing agent. The proximate and chemical analysis of the coal is listed in Table 2. The coal had a high fixed carbon and was relatively low in volatiles, ash, sulfur and phosphorus, making it a good reducing agent for iron oxide reduction. The ash was mainly composed of 39.65% SiO₂ followed by 26.17% Al₂O₃, 12.66% Fe₂O₃ and 11.51% CaO. The iron ore and coal were both crushed to 100% passing 2 mm using a laboratory roller crusher. The particle size distributions of the samples are shown in Table 3, indicating less than 10% of iron ore and coal was in the size range of <0.074 mm. During the storage, the ore and coal samples might absorb moisture in the air, which may affect the reduction. Thus, the crushed samples were dried in a vacuum oven at 353 K for 6 h before each experiment.

Table 1
Chemical compositions of the oolitic iron ore (mass %).

Fe _{total}	FeO	SiO ₂	Al ₂ O ₃	CaO	MgO	P	S	TiO ₂	K	Mn
42.21	4.31	21.80	5.47	4.33	0.59	1.31	0.13	0.19	0.41	0.20

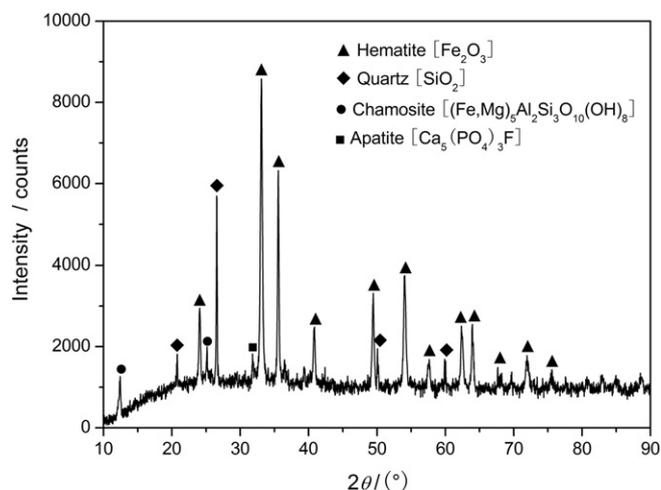


Fig. 1. XRD pattern of the oolitic iron ore.

2.2. Apparatus and procedure

Thermogravimetry (TG), the direct measurement of mass loss during the reaction as a function of time, is one of the most effective techniques to study the reaction kinetics. Thus, TG was used for this study to examine the kinetics of coal-based reduction of the oolitic iron ore. The schematic of experimental apparatus is shown in Fig. 2. The main part of the apparatus was a vertical tube furnace equipped with an automatic balance with a detection precision of 1 mg. The temperature of the furnace was controlled by a temperature controller. The temperatures of the furnace and the reaction zone were measured with two Pt-30%Rh-Pt-6%Rh thermocouples. The accuracy of temperature measurement was ± 1 K. The balance and temperature controller were connected to a computer, which was used to collect the experimental data. An argon gas (99.999% purity) system was used to purge the furnace.

In each reduction experiment, 15-g oolitic iron ore was thoroughly mixed with coal to obtain samples of C/O molar ratios (molar ratio of fixed carbon to reducible oxygen in iron oxides) of 1.5, 2.0, 2.5, and 3.0. The mixture was put into an alumina crucible and a layer of coal (2 g, approximately 3-mm thick) was then placed on the top of the mixture to ensure the reducing atmosphere within the crucible. After that, the furnace was heated to predetermined temperatures (1423 K, 1473 K, 1523 K, and 1573 K) under an Ar gas atmosphere. When the predetermined temperature was reached, the prepared crucible (suspended from the balance arm by platinum wire) was lowered into the center of the reaction tube. During the reduction process, the weight loss over time was continuously monitored and data were recorded by the computer at a time interval of 5 s. The data were then exported to an Excel® spreadsheet for further analyses. Ar gas was injected at a constant flow rate of 1.0 L min⁻¹ (equivalent to ~ 0.2 cm s⁻¹ of linear velocity) and the pressure was kept at constant atmospheric pressure during the experiments.

2.3. Determination of the degree of reduction

The reduction of iron oxides in the oolitic iron ore leads to the weight loss because the reducible oxygen in the crystalline structure of iron

Table 2
Proximate and chemical analysis of coal (mass %).

Fixed carbon	Volatile matter	Ash	P	S	Chemical ingredients of ash				
					SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO
83.64	4.36	11.70	0.004	0.293	39.65	26.17	12.66	11.51	2.14

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