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Reduction of fine iron ore via a two-step fluidized bed direct reduction process

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ABSTRACT

The industrial application of fluidized bed direct reduction (DR) process for fine iron ore is hampered by the sticking of direct reduction iron (DRI) particles. In the present study, the carbon precipitation reaction is coupled with the reduction reaction of fine iron ore to modify the cohesive force among DRI particles. The competition between the reduction reaction of fine iron ore and the carbon precipitation reaction leads to three types of fluidization behaviors: fluidization, unstable fluidization and defluidization. The carbon precipitation reaction is dominant at the temperature below 600–675 °C, and the presence of H_2 could retard the growth of iron whiskers and promote carbon precipitation. A new type of DRI particle covered with carbon shell is therefore constructed and named as DRI_c particle. The growth of iron and carbon gasification can destroy the carbon shell, and lead to the increase of stickiness; however, the presence of CO can retard or prevent the destroying. The C/Fe mass ratio on the surface has significant influence on the stickiness and also the fluidization behavior of DRI_c particles. The lower limit of C/Fe mass ratio, below which defluidization occurs, increases sharply with increasing temperature. Based on these findings, a two-step fluidized bed DR process for fine iron ore is proposed and proved feasible, and the operating lines of the fluidization zones are indicated as maps.

1. Introduction

The world's iron and steel market and its industrial structures have been changing for the last several decades due to rapidly growing demands for direct reduction iron (DRI) and the rise in costs for iron and steel production. In direct reduction (DR) processes, the characteristics and cost of available iron ores play a very important role. The selection of suitable raw materials and DR process will optimize productivity, energy consumption and the overall economy of industrial plants.

Driven by the high cost of raw materials (i.e., lump ore and pellets) and the environmental protection, several fluidized bed DR processes have been developed [1,2]. The main advantage of this technology is that, the fine iron ore, which accounts for about two-thirds of world's iron-ore production, can be charged directly without prior treatment to the process [1]. The bottleneck in the development of fluidized bed DR process is appearance of the sticking of DRI particles. The sticking is intrinsically caused by the sintering of freshly precipitated iron grains, and it can spread out over the whole fluidized bed during very short time. This unintentional agglomeration of particles, which results in that the gas drag force becomes too small to balance the gravitational and buoyancy forces acting on the agglomerations, is the reason for the problem of defluidization that appears in fluidized bed DR processes [3–6].

The sticking tendency of DRI particles is influenced by the adhesive force and the breakage force. The adhesive force is directly proportional to adhesive strength and contact area, while the breakage force is a function of the momentum of the particles, the time of collision and the drag force. A great deal of effort has been made to increase the breakage force and/or reduce the adhesive force, such as increasing the particle velocity [7,8], adding inert components to coat the iron ore particles [4,6,9–12], and limiting the size range of fine iron ore [1]. The addition of inert components, such as MgO, CaO, SiO_2, Al_2O_3, coal and coke particles, may be the most practical and effective method of preventing sticking, but it is not effective for fine iron ore with small size (e.g. less than 0.25 mm) and high metallization degree because of lower kinetic energy and more contact area [13,14]. For example, the mean diameter of the fine iron ore used in the commercial fluidized bed DR process (FINEX process) should be larger than 0.2 mm [1]. Additionally, there are problems with adding inert components into the process, such as high processing cost, high portion of inert material, and separation between DRI and inert material [4].

Since the adhesive feature of DRI particles is the root cause of sticking and defluidization, reducing the stickiness by modifying DRI particles is of key interest, and it may be a general method to avoid defluidization for fluidized bed DR process. It is well known that active iron atom

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generated from the reduction of iron oxides, especially α-Fe_2O_3, is a catalyst for Boudouard reaction [15,16]. This catalytic reaction provides a way to reduce the stickiness of DRI particles via carbon precipitation. An investigation of Neuschütz [13] suggests that carbon deposition as a counter-measure against sticking of fine iron ore seems to be effective with different ores and even for extremely small particle fractions, and pellet feed coated with carbon can be completely metallized without sticking at the temperatures of 850–900 °C. An investigation of Zhang et al. [17] suggests that the carbon element deposited on the surface of Fe_2O_3 particles is in the forms of graphitic and Fe_3C, and the prevention of sticking at 900 °C is attributed to graphitic carbon. However, the fluidization behavior and reduction behavior of fine iron ore, where the reduction reaction and the carbon precipitation reaction are coupled, are scarcely studied. For now, this method has not been applied in fluidized bed DR process because the control mechanism of fluidization behavior is not well understood.

The aim of this present work is to investigate the modification of DRI particles by carbon precipitation and its influence on the fluidization behavior and the reduction behavior of fine iron ore particles in fluidized bed. More specifically, the experimental parameters affecting carbon precipitation rate, including gas composition, operating temperature and metallization degree, are investigated in detail. The morphology, structure and phase change during reduction are obtained, through which fundamental insights into the fluidization behavior and the reduction behavior of modified DRI particles are provided. Finally, a process for DRI production based on the reduction reaction and the carbon precipitation reaction is proposed and is experimentally proven. The present paper reports our first findings.

2. Experiment

2.1. Raw materials

The chemical compositions of the fine iron ore supplied by Vale of Brazil are given in Table 1. The fine iron ore with diameter range of 106–150 μm [(−45 + 60) mesh TYLER size fraction] was used in all the reduction experiments. Its true density is about 4939 kg/m^3 and the bulk density is about 2209 kg/m^3. The H_2 and N_2 gases used for reduction were of 99.999% purity, and the CO gas was of 99.99% purity. All the gases were supplied by Beijing Huayuan Gas Chemical Industry Co. Ltd.

2.2. Experimental apparatus

The experimental apparatus is shown in Fig. 1. The bubbling fluidized bed reactor with inner diameter of 16 mm was made of quartz, and there were holes for measuring the temperature of the reaction zone and the pressure drop across the bed. The facility was surrounded by an electric resistance furnace, and the bed temperature control was achieved by a PID controller. The gas flow rates and pressure drop across the bed were measured by several digital mass flow controllers and a differential pressure sensor, respectively.

2.3. Experimental procedure

The fluidized bed reactor, which was loaded with approximately 8 g of ore, was first purged with N_2 gas at fluidized condition, and then placed into the furnace. When the aimed reaction temperature was attained, the purging stream was switched to the reducing gas so as to reduce the iron ore. The fluidization was carried out at atmospheric pressure. The total gas (N_2 or H_2–CO mixture) flow rate was set to 1.5 l/min at the standard state, and the superficial velocity, which depended on the experimental temperature, varied between 0.3 and 0.5 m/s. The bed was operated at bubbling fluidization regime.

Table 1
Chemical composition of Brazil iron ore in mass%.

Composition	TFe	Fe_2O_3	FeO	SiO_2	CaO	MgO	Al_2O_3
[Mass%]	68.94	96.80	0.72	1.98	0.10	0.10	0.30

At the predetermined time, or at the time when defluidization occurred, the reducing gas stream was switched back to N_2 gas, and the reactor was removed from the furnace. Then the reduced iron ore sample was cooled down under N_2 atmosphere to the ambient temperature, and transferred into zipper seal sample bag full of N_2 gas in an effort to prevent reoxidation.

The carbon contents of the reduced samples were measured by a carbon–sulfur analyzer (LECO CS-344, USA). The degree of metallization (MET) is calculated on the basis of the chemical analysis of the reduced iron ore sample for the moles of total iron (Fe_{tot}) and metallic iron (Fe^0) as follows [2]:

$$\mathrm{MET} = \mathrm{Fe}^0/\mathrm{Fe}_{tot} \times 100 \quad \text{in} \quad [\%] \tag{1}$$

where, both Fe^0 and Fe_{tot} are determined by the titrimetric method according to National Standard GB 223.7-2002 of China, and the iron of cementite is included in Fe^0.

Since the MET value of 100% can hardly be achieved, the value of 90% is adopted as the sign that the reduction of iron ore is nearly complete. For the cases of defluidization, the experiments were ended at the defluidization time, and for the other cases, the experiments were ended until the reduction is nearly complete.

The phase compositions were characterized using X-ray diffractometer (XRD, X' Pert MPD Pro, PANalytical, the Netherlands) with the Cu K_α radiation ($\lambda = 1.5408$ Å). The microstructure of the iron ore and reduced samples was observed by a field emission scanning electron microscope (FESEM, JSM-7001F, JEOL, Japan), and the elemental concentration on the surface was analyzed by an associated energy dispersive X-ray spectroscopy (EDS, X-Max, Oxford Instruments, England).

An investigation of Schouten and Van den Bleek [18] demonstrates that if defluidization occurs, part of the bed mass will no longer be involved in the fluidization process, which will lead to a lower bed-pressure drop. The easiest way to detect defluidization seems to be the recording and evaluation of the average bed-pressure drop. To distinguish the feature of different fluidization behaviors, the raw data of bed-pressure drop were smoothed using the 'smooth' function in MATLAB. The time where defluidization occurred was recorded as the defluidization time (t_{def}).

3. Results

3.1. Reduction behavior of fine iron ore

The metallization curves of the iron ore reduced by pure H_2 at different temperatures are plotted in Fig. 2. Defluidization occurred at all the experimental temperatures during metallization of iron ore because of sticking. As the temperature increased, the adhesive strength among DRI particles increased sharply, so the MET of defluidized iron ore at higher temperature is lower. It is clear that the reduction was generally enhanced by the rise in temperature. Thus, the defluidization time decreased sharply with increasing temperature.

The metallization curves of the iron ore reduced by pure CO and 80% H_2–20% CO mixture, and the corresponding carbon precipitation curves at different temperatures are plotted in Figs. 3 and 4, respectively. The metallization curves indicate that the reduction was faster at the early stage and slowed down at the later stage. The reduction rate seemed to be sensitive to the gas composition, and the reaction proceeded faster with H_2 than CO. For this series of experiments, the thermodynamic