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Direct reduction of hematite powders in a fluidized bed reactor

Qingshan Zhu [a,*], Rongfang Wu [a,b], Hongzhong Li [a]

[a] State Key Laboratory of Multiphase Complex Systems, Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100190, China
[b] Graduate University of Chinese Academy of Sciences, Beijing 100049, China

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ABSTRACT

Ultrafine hematite powder was reduced to produce ultrafine iron powder in a 50%Ar–50%H_2 atmosphere at 450–550 °C in a fluidized bed reactor. The ultrafine hematite powder shows the typical agglomerating fluidization behavior with large agglomerates fluidized at the bottom of the bed and small agglomerates fluidized at the upper part of the bed. It was found that defluidization occurred even at the low temperature of 450 °C with low metallization rate. Defluidization was attributed mainly to the sintering of the newly formed iron particles. Granuation was employed to improve the fluidization quality and to tackle the defluidization problem, where granules fluidized like a Geldart's group A powder. Granulation was found to effectively reduce defluidization during reduction, without however sacrificing reduction speed. The as-reduced iron powders from both the ultrafine and the granulated hematite exhibited excellent sintering activity, that is, fast sintering at temperature of as low as ~580 °C, which is much superior as compared to that of nano/ultrafine iron powders made by other processes.

1. Introduction

In recent years, there are increasing demands for ultrafine iron powder in powder metallurgy, chemical engineering, and environmental industries (Faiola et al., 2011; Goswami, Deb, Thakur, Sarma, & Basumallick, 2011; Pranda, Hlavacek, & Markowski, 2001) due to its high chemical and sintering activity. Conventional processes such as the Hoganas process and the water atomization process could not produce ultrafine iron powder. Various new technologies have therefore been developed to produce ultrafine iron powder, such as high energy ball milling (Zdujic et al., 1998), vacuum evaporation (Lee, Jang, Kim, Tolochko, & Kim, 2005), sputtering (Munoz-Martin, Prieto, Ocal, Martinez, & Colino, 2001), liquid phase reduction (Ohno, Kaimoto, Maeda, Nishioka, & Shimizu, 2011), levitation melting method in liquid nitrogen (Kecskes & Woodman, 2003). These technologies are however not suitable for producing ultrafine iron powder at large scale because of high cost, complex devices or extreme reaction conditions. Therefore, it is necessary to develop new processes that have the potential of producing ultrafine iron powder at large scale.

Fluidized bed reactors have been used to reduce iron ore to manufacture direct reduced iron or hot-compacted iron with capacities of over 1 million tons per year per unit (Anameric & Kawatra, 2009; Schenk, 2011). They are therefore considered to have great potential to produce ultrafine iron powder at large scale. Two major obstacles need to be overcome before high-efficiency production of ultrafine iron powder can be realized using fluidized bed reactors. First, ultrafine powders are difficult to fluidize homogenously (Huang et al., 2010; Kusakabe, Kuriyama, & Morooka, 1989; Valverde et al., 2008). It is therefore necessary to find ways to improve the fluidization quality of the reduction process. Second, during direct reduction, defluidization frequently occurs due to sticking of the newly formed iron particles (Hayashi & Iguchi, 1992; Komatina & Gudenau, 2004). Defluidization is affected by many factors, such as the type of ore, reduction degree, reduction temperature, and particle size, and the tendency of defluidization was found to increase with decreasing particle size (Komatina & Gudenau, 2004). To our best knowledge, direct reduction of ultrafine iron oxide powders via fluidized beds to produce ultrafine iron powders has not yet been reported.

In the present study, ultrafine hematite powder was employed to study the fluidization/defluidization behavior in a lab-scale fluidized bed using a hydrogen–argon mixture. Granulation of the ultrafine hematite powder was used to solve the defluidization problem during reduction. The sintering activity of the reduced ultrafine and granulated iron powder was also characterized.

2. Experimental

2.1. Materials

The ultrafine hematite powder used in the present study has an average diameter of 246.0 nm (99.9 wt% Fe_2O_3, Sinopharm

* Corresponding author. Tel.: +86 10 62536108; fax: +86 10 62536108.
E-mail address: qszhu@home.ipe.ac.cn (Q. Zhu).

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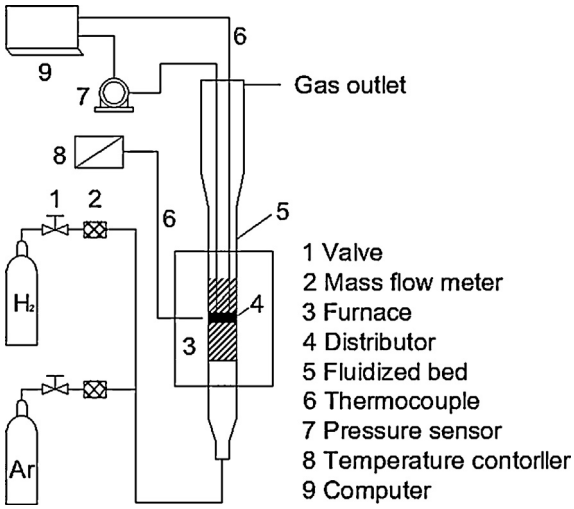

Fig. 1. Schematic of fluidized bed reduction system.

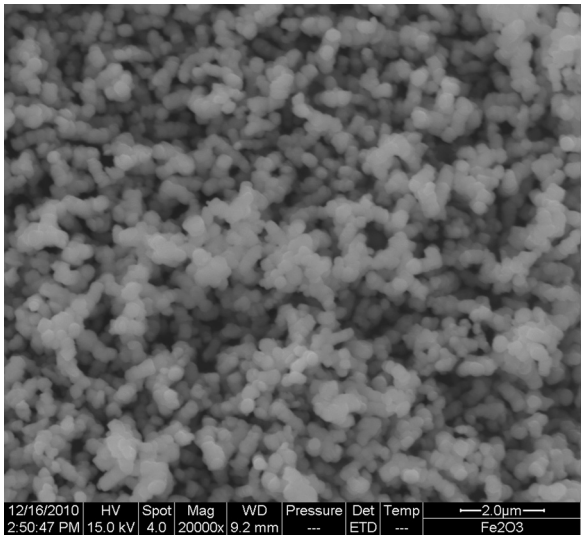

Fig. 2. Typical microstructure of the ultrafine hematite powder.

Chemical Reagent Co. Ltd., Beijing, China). Granulation was performed by first mixing the hematite powder with water at ambient temperature, followed by drying at 120 °C and sintering in air at 900 °C for 6 h using a muffle furnace (SRJX-4-3, Tianjin Zhonghuan Laboratory Electric Co. Ltd., Tianjin, China). The as-sintered powder was then crushed and sieved to the size of 150–180 μm, which was used as the granulated powder.

High purity argon and hydrogen (purity 99.99%, Beijing Huayuan Gas Chemical Industry Co. Ltd., Beijing, China) were used as received without further purification.

2.2. Experimental

The experimental setup is illustrated in Fig. 1. The fluidized bed reactor is made of quartz glass, with a height of 870 mm and an inner diameter of 16 mm, using a porous sintered quartz glass plate as the gas distributor. Reduction of the hematite powders was performed in a 50%Ar–50%H_2 gas mixture at 450–550 °C, while the fluidized bed reactor was heated up by a home-made vertical electric furnace. The gas flow rate was fixed at 1.0 L/min (0.5 L/min Ar + 0.5 L/min H_2) at the standard state for both the ultrafine and the granulated powders and was controlled by two mass flowmeters (D08-3B, Beijing Sevenstar Electronics Co. Ltd., Beijing, China). A pressure sensor was installed above the distributor for on-line monitoring of bed pressure drop during fluidization. For reduction experiments, the hematite powder was first fluidized with argon before the bed was directly moved to the hot zone of the furnace already at the set temperature. When the sample reached the set temperature as measured by the inserted thermocouple, the reducing gas mixture was introduced to the reactor. After the desired time of reaction, the reactor was removed from the hot zone of the furnace and quenched directly by spraying water on its outer surface, and then, the as-reduced iron powder was collected and subjected to various characterizations.

2.3. Sample characterization

The metallization degree η of the hematite sample is defined as

$$\eta = \frac{M_{Fe^0}}{M_{Fe}} \times 100, \quad (1)$$

where the M_{Fe^0} and M_{Fe} are the metallic iron content and the overall iron content of a sample, respectively. Both M_{Fe^0} and M_{Fe} are determined by the titrimetric method according to National Standard GB 223.7-2002 of China.

The phase compositions were characterized using X-ray diffractometry (XRD, X' Pert MPD Pro, PANalytical, the Netherlands) with the Cu K_α radiation (λ = 1.5408 Å). The microstructure of the reduced samples was observed by a field emission scanning electron microscope (FESEM, Quanta 200, FEI, the Netherlands).

The as-reduced iron powders were uniaxially pressed to form cylinders of ϕ 5 × 2 mm^3 under 1000 MPa for 60 s. The cylinder was used to study the sintering behavior of the reduced iron powders under hydrogen atmosphere via a dilatometer (L75/1550, LINSEIS, Germany) with a heating rate of 10 °C/min from room temperature up to 1000 °C. The density of the sintered compacts was then calculated according to the green density and the measured linear shrinkage by the following equation:

$$\rho = \frac{\rho_0}{(1 + \Delta L/L_0)^3}, \quad (2)$$

where ρ_0 is the density of a green compact determined from its weight and geometric dimensions, L_0 is the original height of the cylinder, and $\Delta L = L - L_0$, where L is the instantaneous cylinder height measured by the dilatometer. A reduced iron powder (Product No. 7439-89-6, Shantou Xilong Chemical Factory Co. Ltd., Shantou, China) was also employed to test the sintering behavior for the purpose of comparison.

3. Results and discussion

The hematite powder used in the present study is submicron in size and spherical in shape, as shown in Fig. 2, and belongs to the Geldart group C powder (Geldart, 1973). Fluidization of the hematite powder is difficult: with increasing gas velocity, the bed experiences slugging, channeling, disrupting, and finally, at high superficial gas velocity, stable agglomerating fluidization took place, with big agglomerates in the bottom and small agglomerates in upper parts of the bed, as commonly observed for the fluidization of ultrafine powders (Li, Lu, & Kwauk, 2003).

The ultrafine hematite powder was directly reduced in a 50%Ar–50%H_2 gas stream at 450–550 °C. Fig. 3(A) illustrates the variation of pressure drop with time of reduction at three different temperatures, and Fig. 3(B) shows the time of defluidization and the metallization rate at defluidization. The figure shows two