Powder Technology 241 (2013) 142–148

Contents lists available at SciVerse ScienceDirect

Powder Technology

journal homepage: www.elsevier.com/locate/powtec

Prevention of agglomeration/defluidization in fluidized bed reduction of Fe_2O_3 by CO: The role of magnesium and calcium oxide

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ARTICLE INFO

Article history:
Received 22 November 2012
Received in revised form 18 February 2013
Accepted 18 March 2013
Available online 26 March 2013

Keywords:
Fluidized-bed reduction
Fe_2O_3
Prevention
Defluidization
Magnesium/calcium oxide

ABSTRACT

Influence of magnesium and calcium oxide on control of agglomeration and defluidization during Fe_2O_3 reduction was investigated in a visual fluidized bed reactor. Added MgO and CaO extended the defluidization time and thus inhibited agglomeration significantly. According to the controlled defluidization tests, the particle cohesiveness and agglomeration tendency of bed materials were reduced by adding MgO and CaO. And the inhibition of MgO was more effective. However, the inhibition effect was reduced with increasing the operating temperature. The coating layers of bed particles were examined by the scanning electron microscope/energy-dispersive spectroscopy (SEM/EDS), coupled with X-ray diffraction (XRD). Results showed that a coating layer on the surface was composed of magnesio-wustite (MgO·FeO) and calcio-wustite (CaO·FeO) generated by the reactions between Mg/Ca oxides and Fe_2O_3/FeO. During reduction process this coating layer was difficult to reduce and thus suppressed the connection of precipitated iron. Consequently, the bed particles became less sticky and avoided the surfaces of bed particles to adhere.

1. Introduction

Fluidized beds are satisfactorily suited to processing the finely sized raw materials, due to good solid mixing, high heat transfer, and large contact surface area, etc. Therefore fluidized beds have been applied in many industrial processes. For the recent metallurgy process, fluidized bed reactors are used as reduction or pre-reduction equipment to produce metallic iron by reducing iron ore (Fe_2O_3) with gas reductant (i.e. CO, H_2, CH_4). However, in the practical operations, the bed agglomeration which can result in the uncontrollable shutdown of fluidized bed reactors has become a serious problem [1–3]. The continuous operation and high productivity are often limited by partial or complete defluidization. Therefore, particle agglomeration in fluidized bed systems has received extensive research attention.

Many factors can result in bed materials to undergo agglomeration and defluidization. Gluckman et al. [4] indicated that the generation of agglomerations depended on the cohesiveness of particle collisions. Seville [5] pointed out that the defluidization phenomenon was attributed to an increased rate of sintering at elevated temperature, and the tendency of particle to agglomerate depended strongly on their physical and chemical characteristics at high temperature. For fluidized-bed reduction of iron ore, the sticking occurred mostly during metallization of ore and was controlled by a combination of several factors such as iron morphology, surface energy of iron, and external shape of ores [6–8]. Some ore particles were precipitated by the metal iron with the fibrous shape on the particle surface. The sticking was initiated by the contact of the needles that hooked mechanically the particles together. And the work of Gransden et al. [8,9] showed that the sticking was associated with the iron–iron contact regardless of formation of iron whiskers or not. Zhong et al. [10] also reported agglomerates formed due to sintering of reduced iron, and nano/mirco-structure on the surface of particle had a promotive effect on defluidization.

For the purpose of preventing defluidization, some literatures reported that various elements markedly affect the agglomeration/defluidization during incineration and reduction, including sulfur, alkali metals and alkali earth metals [11–13]. Most researches focused on the additive coating and the relationship between the additives and precipitated iron morphologies on agglomeration/defluidization. The additive elements (Mg, Ca, Si, K, Na etc.) can produce drastic morphology changes to cause iron whisker formation due to increasing the diffusion rate of Fe [14–16]. Three mechanisms of defluidization prevention were mainly considered: (1) Formation of eutectics or compounds with high melting points. (2) Added metal elements change the morphology of precipitated iron and suppress the growth of iron whiskers. (3) Formation of an inert coating to avoid the adhesion of precipitated iron. Previous works [3] have proven that for iron ores with higher amount of gangue (MgO, CaO, Al_2O_3, SiO_2) the agglomeration tendency is smaller. So the control of fluidized bed agglomeration/defluidization

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http://dx.doi.org/10.1016/j.powtec.2013.03.030

by adding inert materials was investigated widely due to availability and simplicity. Hayashi et al. [13] studied the use of inert oxides (Al_2O_3, MgO, CaO, SiO_2) as coating materials by water-slurry method to reduce the defluidization conditions. The results showed that Al_2O_3 and MgO were effective additives to avoid defluidization due to the physical spacer effect on the surface. And the coverage Al_2O_3 and MgO reduced the surface energy of iron for particle agglomeration. The coating methods by adding oxides to prevent defluidization in fluidized reduction of Fe_2O_3 were considered mainly to be the effects of physical coating. However, the alkali earth metals (Mg and Ca) may also react with Fe_2O_3 to form the ferrite compounds, which would have inhibition or promotion effect on agglomeration. Therefore, the chemical behavior of added elements was also important in the defluidization characteristic of fine particles. Unfortunately how the added elements behaves chemically on Fe_2O_3 surface during fluidized-bed reduction is not fully known, which is of importance in understanding the prevention mechanism of defluidization. Therefore, it is necessary to clarify the chemical behavior of additive elements in the formation of coating layers.

In this work, the artificial Fe_2O_3 was used to eliminate the interference from other elements and thus elucidate the effect of earth alkali metals (Mg and Ca) on agglomeration/defluidization during Fe_2O_3 reduction. As for the prevention mechanism of bed agglomeration, we focus on the formation processes of coating layers, especially the chemical phase transitions of additive elements in the reduction process.

2. Experimental

2.1. Apparatus and materials

The experimental apparatus is shown in Fig. 1. The visual reactor is a bubbling fluidized bed, consisting of a transparent silica tube with an inner diameter of 2.5 cm. The facility was surrounded by transparent electric resistance, so that the fluidized state within reactor can be observed intuitively at high temperature. Bed temperature control was achieved by a PID controller driven by a thermocouple constantly immersed in the fluidized bed. The gas flow rate and pressure drop across the bed were measured by a digital mass flow controller and a pressure transmitter.

The artificial Fe_2O_3 particles as bed material were produced by crushing after annealing Fe_2O_3 fine powder (>99%, 10 μm) for 48 h at 1200 °C. The samples were divided into three particle grades: 50–74, 74–149 and 149–210 μm by sieving. In this experiment, the Mg and Ca species were added to test the inhibition or promotion for defluidization. To simulate the effect of alkali earth metals on agglomeration and defluidization and the formation of coating layer during reduction, the Mg and Ca species were added as a metal solution formed from metal nitrates dissolved in distilled water. The metal nitrates were $Mg(NO_3)_2$ and $Ca(NO_3)_2$. The Mg/Ca solution (5 mL) is then added to the Fe_2O_3 particles (5 g). Before experiment, the samples were stirred and dried to make sure the Fe_2O_3 particles can absorb the metal solution completely. After that, the Mg/Ca-added samples were heat-treated by N_2 in fluidized bed at 800 °C for 2 h. The metal nitrates decomposed to form MgO/CaO on the surface of Fe_2O_3 particles. The weight percentage of added elements was calculated as the ratio of metal oxides. The additive content is the mass ratio of MgO/CaO in Fe_2O_3.

2.2. Gas-fluidization reduction and defluidization test

The Fe_2O_3 particles were first fluidized in pure N_2 to preheat. When the sample was up to the predetermined reducing temperature, the fluidizing agent was switched to mixed gas (CO/N_2 = 1:1). The operating velocity was about 15–20 times that of the minimum fluidization velocity. Point of bed defluidization was determined by pressure drop profile and visual observation. Defluidization is defined as any condition where a well-fluidized bed loses fluidization, whether partial or total [17]. As the defluidization occurred, a rapid decrease in the bed pressure drop was observed and this time was defluidization time. The typical pressure drop vs. time diagram was shown in Fig. 2. When defluidization occurred, the experiment was stopped and the defluidization time was recorded. The bed sample was cooled to the room temperature in inert atmosphere. Then the reduced particles were analyzed by scanning electron microscopy (SEM, JSM-6700F)/energy dispersive spectrometry (EDS, Noran System six) and X-ray diffraction (XRD, X'Pert PRO MPD). The metallization degree (M_{Fe}) of the reduced samples was measured using chemical titration analysis [10], which was defined as:

$$M_{Fe} = \frac{m}{m_0} \times 100\%$$

where m and m_0 are the mass of metallic iron and total iron respectively.

2.3. The controlled bed defluidization test

To determine the bed agglomeration tendencies, the controlled bed defluidization tests were carried out. Each experiment was started by normal fluidized-bed reduction at 700 °C. At a point where approximately a designated metallization degree was achieved by controlling

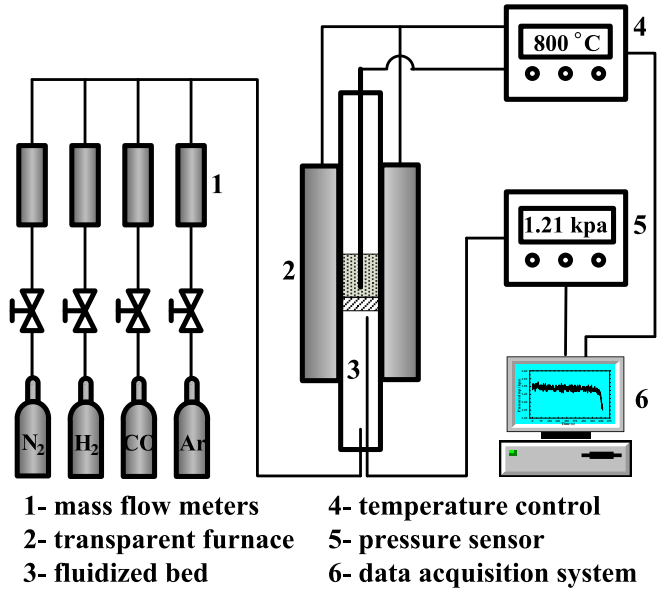

Fig. 1. Schematic diagram of fluidized bed apparatus.

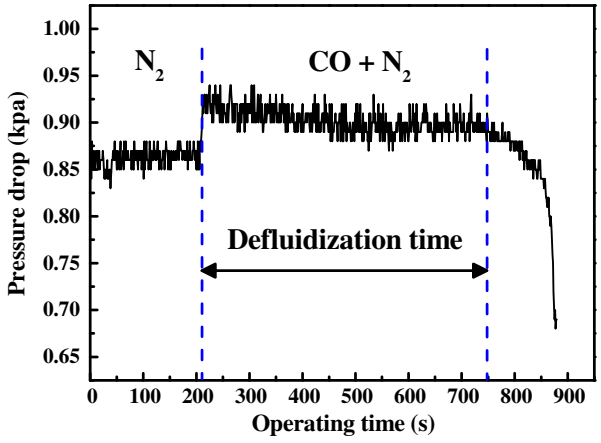

Fig. 2. The typical plot of pressure drop vs. time in fluidized reduction of Fe_2O_3.