Powder Technology 338 (2018) 365–375

Contents lists available at ScienceDirect

Powder Technology

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

Preparation of core-shell iron ore-biochar composite pellets for microwave reduction

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ARTICLE INFO

Article history:
Received 12 April 2018
Received in revised form 7 July 2018
Accepted 9 July 2018
Available online xxxx

Keywords:
Biochar
Composite pellets
Microwave
Inhomogeneous distribution
Core-shell structure

ABSTRACT

Due to its high carbon and low impurities contents, as well as good reactivity, biochar can partly or totally replace coal or coke as a promising reducing agent in metallurgy. This study offers a new method to produce qualified metallized pellets for steelmaking after microwave-assisted self-reduction of iron ore-biochar composite pellets. The key point was to prepare green composite pellets with good quality indexes which also allowed sufficient self-reduction under microwave irradiation. For this purpose, core-shell iron ore-biochar composite pellets were prepared with inhomogeneous biochar distribution. It was found that high grade iron concentrates A and B could be used together for improving pelletizing. Controlling the distributions and proportions of iron concentrate B (different additions in the core and shell) and biochar (all located in the core of the pellets) would contribute to high-quality iron ore-biochar green composite pellets with the drop number of 3.6 times/0.5 m, compressive strength of 11.1 N/p, and decrepitation temperature of 410 °C under the pelletizing conditions of total proportion of iron concentrate B of 30%, pelletizing time of 16 min, rotation speed of 25 r/min, bentonite dosage of 2.3%, C/Fe mass ratio of 0.225, pellet moisture content of 13.0%, and proportions of iron concentrates A and B in the shell of 10% and 0%, respectively. The subsequent microwave reduction tests showed that the core-shell metallized pellets with the total iron content and metallization degree of 89.15% and 95.52%, respectively, could be obtained after microwave reduction at 1050 °C for 30 min under N_2 atmosphere. They had better reduction indexes than those produced from the pellets with homogeneous structure, serving as a good burden for steelmaking directly.

1. Introduction

China is the country with the largest production and consumption of crude steel in the world. Due to the use of fossil fuel (e.g., coal and coke) in the traditional blast furnace ironmaking process, greenhouse gases (e.g., CO_2), toxic gases (e.g., SO_2 and NO_x) and metallurgical dusts are discharged massively and have caused serious pollution to the environment [1–3]. According to the statistics of the World Steel Association, the crude steel production in China in 2017 was 0.8317 billion tons [4], a year-to-year growth of about 5.7% compared with 2016. The blast furnace process consumed 48.17% of energy in iron and steel enterprise [5]. Along with the 800 million tons of pig iron output in 2016, about 1 million tons of flue gas dust, 1.8 million tons of SO_2 and about 0.6 million tons of NO_X were discharged in the blast furnace ironmaking process [6]. It poses a huge challenge to the environmental protection and resources utilization.

In order to seek the sustainable development of iron and steel metallurgy, non-blast furnace ironmaking technologies, such as direct reduction ironmaking (DRI) process, become a research hotspot [7–9] as they produce burden (e.g., metallized pellets) for steelmaking directly. Compared with the gas-based DRI process, the coal-based DRI process, such as reduction of carbon-containing pellets which have the characteristics of fast self-reduction, stable chemical composition, good metallurgical properties, uniform size, easy preparation and high productivity, has been wildly studied in recent years [10]. It is considered more suitable for China since the country has abundant coal but scant domestic natural gas resources [5,11,12].

For preparation of carbon-containing pellets, most of previous studies focused on the use of pulverized coal and coke, which did not effectively change the raw material structure with fossil fuels, still causing large emissions of SO_2, NO_X, and CO_2 in the ironmaking process. Biochar is formed by the pyrolysis of renewable biomass in nature at high temperatures, representing a renewable fuel with the unique characteristic of carbon neutrality [13,14]. Compared with coal, biochar has high fixed carbon content (30%–90%), low impurities (e.g., S and P) contents

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https://doi.org/10.1016/j.powtec.2018.07.037
0032-5910/

[15] and large surface area (60–350 times larger than that of coal [16] and over 10 times larger than that of coke with the same particle size [17]) which favor the reduction [18]. In the gasification performance, it was shown that compared with pulverized coal, biochar had higher chemical reactivity, faster reaction rate and lower activation energy when gasified, which greatly promoted the direct reduction of iron oxide [19]. In the reduction of pellets, a certain amount of volatiles in biochar could be pyrolyzed to H_2 and C_xH_y at lower reaction temperatures (<900 °C) which accelerated the reduction rate of iron oxides and improved the reduction degree to some extent (7%–8%) [15,20]. In addition, due to its low contents of ash, S, P and other impurities, the use of biochar could reduce the emission of SO_2, NO_x and dust [21,22] and the addition of fluxes in ironmaking and steelmaking [23]. Also, as a carbon source, biochar may play an important role in the growth of metallic iron grains during the reduction of carbon-containing pellets. A previous study on the gasification reaction of biochar showed that in comparison with blast furnace coke and petroleum coke, biochar had smaller activation energy (decreased by about 10 kJ/mol) and lower reaction temperatures of gasification in CO_2 atmosphere [24]. The fast reaction rate promoted the formation and growth of iron whiskers in the reduction process of pellets, enhancing the strength of metallized pellets.

Along with the use of biochar in producing the metallized pellets, microwave as a clean energy has been applied for pellets reduction [25,26] as iron ore and carbon are both strong microwave absorbers [27]. Due to its long wavelength and dependence on material properties (microwave permittivity and permeability), microwave energy can heat the material volumetrically and selectively. It has the potential to remove temperature gradient that often occurs in the conventional reduction process, contributing to high reduction rate and rapid growth of newly generated iron grains. However, to date there is no systematic research on microwave reduction of biochar-containing pellets [27,28].

The main purpose of this study was to offer a novel method for preparation of appropriate green core-shell iron ore-biochar composite pellets for fast production of qualified metalized pellets using microwave energy for steelmaking. The green composite pellets were firstly prepared with consideration of requirements of their quality indexes and impedance matching in microwave self-reduction by adjusting their structure and various pelletizing parameters, including type of iron concentrate, pelletizing time, rotation speed of disc pelletizer, dosage of bentonite, C/Fe mass ratio, moisture content, and the distribution of iron concentrate in the shell of pellets. This was followed by self-reduction of the composite pellets under microwave irradiation, which produced qualified metallized pellets as burden for steelmaking, featured by better reduction indexes than those produced from the pellets with homogeneous structure.

2. Experimental

2.1. Raw materials

2.1.1. Iron concentrates

Two types of iron concentrates, A and B, were used for the preparation and microwave reduction of iron ore-biochar composite pellets. Their main chemical compositions are shown in Table 1. Iron concentrate A was a major raw material with high iron grade (67.61%) and low hazardous elements, such as K, S and P, meeting the chemical composition requirements for DRI. Preliminary pelletizing tests showed that A was not suitable for pelletizing (see analysis below) and the other high grade iron concentrate B was used and mixed with iron concentrate A for preparation of qualified green composite pellets. As can be seen from Table 1, both iron concentrates A and B belonged to magnetite with FeO content of 20.06% and 27.47%, respectively. Considering the higher iron content of iron concentrate A than iron concentrate B, increasing usage of A with minimal addition of B would be of benefit to the production of high grade metallized pellets after reduction.

The particle size distributions and specific surface areas of iron concentrates A and B are shown in Table 2. As can be seen from Table 2, the contents of −0.074 mm (−200 mesh) and − 0.045 mm (−325 mesh) particles of iron concentrate A were 92.29% and 83.28%, respectively, while for iron concentrate B the counterparts were 99.51% and 90.33%, respectively. As the required content of −0.074 mm particles of iron concentrate in practical production is 85% [29], neither iron concentrate A nor iron concentrate B needs to be pretreated before pelletizing. The specific surface areas of iron concentrates A and B were 1716 cm^2/g and 903 cm^2/g, respectively. It should be mentioned that ultrafine particle size and narrow particle size distribution are not conducive to the formation of proper water capillary radii in pellet after pelletizing, which would impact the thermal stability and thus the structure integration of pellets during reduction due to water evaporation. From this perspective of view, the combined use of concentrates A and B with different specific surface areas would improve the quality of the green composite pellets.

The microstructures of iron concentrates A and B are shown in Fig. 1. As can be seen from Fig. 1, the surface of the iron concentrate A was coarse and the particles were mainly irregular, which would facilitate their embedment and adhesion with other raw materials during pelletizing, promoting pelletizing performance. Compared with iron concentrate A, iron concentrate B had smaller size and smoother surface of particles, in agreement with its lower surface area in Table 2. The findings confirmed that the combined use of iron concentrate A and B was suitable for pelletizing.

Table 3 lists the pelletizing properties and other physical properties of iron concentrates A and B, including the maximum capillary water content, migration velocity of capillary water and pelletizing index (K). It shows that the pelletizing indexes of iron concentrates A and B were, respectively, 2.76 and 0.93, indicating their excellent pelletizing properties ($K > 0.8$) [29]. As iron concentrates A and B received by the test were pre-dried, they had low migration velocities of capillary water (3.81 mm/min and 4.72 mm/min, respectively), which would cause slow pellet growth. Therefore, before pelletizing, iron concentrates A and B must be pre-wetted to meet the production requirements of green composite pellets.

2.1.2. Biochar

The biochar used in this study was pyrolyzed from oak, which was a kind of hardwood with high content of cellulose suitable for making biochar. During the pyrolysis, the dried oak was loaded into a muffle furnace and then heated to 550 °C with a ramp rate of 2 °C/min and pyrolyzed for 2 h. The yield of biochar was 32.8%. To obtain a suitable granularity for pelletizing, the biochar was ground in advance using a Raymond mill. The chemical composition of biochar is shown in Table 4. It had high carbon content (80.76%) and low H, O, N and S contents (0.48%, 4.31%, 0.32% and 0.02%, respectively), indicating its low potential impact on the environment. According to its proximate analysis, the contents of fixed carbon (C_{ad}), volatile (V_{ad}) and ash (A_{ad}) were

Table 1
Main chemical compositions of iron concentrates.

Sample	Content (wt%)										
	TFe	FeO	SiO_2	CaO	MgO	Al_2O_3	K_2O	S	P	Pb	Zn
A	67.61	20.06	1.53	0.84	0.34	0.65	0.028	0.01	0.067	–	–
B	65.56	27.47	3.32	1.13	0.42	0.19	0.33	0.084	0.023	0.0098	0.0092