

A STUDY OF DIRECT REDUCTION CHARACTERISTICS OF BAYER PROCESS RED MUD-COAL COMPOSITE PELLETS

by

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The effects of reduction temperature, particle size, pellet diameter, and the ratio on the reduction rate in red mud-coal composite pellets were studied. The iron phase change of the reduction under different temperatures was analyzed applying X-ray diffraction technique. The microstructure of reduction was investigated using scanning electron microscope. The conclusion of the study is that the reduction reaction rate increased rapidly with the increase of reduction temperature. The reduction of Fe_2O_3 forming Fe_3O_4 started under 700 °C. At 1100 °C, the red mud-coal composite pellets with carbon and oxygen mole ratio 1:1 obtained a good reduction result. The appearance of metal iron and the clear porous structure indicated that the reduction had developed to a high degree.

Key words: direct reduction, composite pellets, Bayer process red mud, reduction characteristics

Introduction

The direct reduced iron plays a more and more significant role in the iron and steel industry [1]. The direct reduced iron has excellent performance in reducing the use amount of coke, environmental protection, etc. The reduction process is a gas-solid reaction, which has been widely studied by a large number of scholars in the past few decades [2-13]. This work mainly focuses on the process condition experiments, saving energy and reducing material consumption. Due to the low grade of iron and the shortage of natural gas, the research mainly focuses on the recovery of low grade and coal-based direct reduction in China. In this study, Bayer process red mud is used for production of direct reduced iron. The effect of temperature, particle size and pellet diameter on reduction characteristics and the morphology in red mud-coal composite pellets are analyzed.

Materials and experiments

The red mud used in this study was obtained from Shandong. The chemical constituents of red mud is shown in tab. 1. The bituminous coal was obtained from Shanxi. The main reductant composition were ash is 13.0%, volatile matter is 12.5%, and fixed carbon is 74.5%, and the particle sizes distribution are shown in tab. 2.

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Table 1. Chemical constituents of red mud (w/%)

TFe [%]	FeO [%]	SiO ₂ [%]	CaO [%]	Al ₂ O ₃ [%]	MgO [%]	S [%]
49.21	1.02	10.98	0.76	10.02	0.68	0.05

Table 2. Particle size distribution (w/%)

Particle size distribution [μm]	Quality percentage [%]
75~150	52.32
45~75	34.16
38~45	13.52

The mean particle size of bituminous coal was 150 μm. Pellets were made from red mud-coal mixture and 2% bentonite binder in a disc pelletizer. Then the red mud-coal composite pellets were dried in drying oven at 105 °C for 24 hours to wipe off the free moisture, and these pellets were heated at 700~1100 °C in nitrogen atmosphere with a flow of 1 L/min. The quality of the samples was measured by electronic balance and recorded every one minute. The reduction reaction was carried through a vertical furnace which comprised a temperature controller, a gas distributor disc, an electronic balance, and a quartz glass tube reactor. Nitrogen was passed into the vertical furnace to prevent the oxidation atmosphere at the beginning of the experiment. When the desired experiment temperature was reached, the red mud-coal composite pellets were placed in the heating zone. The pellets were suspended under the electronic balance.

The total mass loss of the pellets were measured continuously and the value was transformed into reduction fraction f which was defined as the following formula [14]:

$$f = \frac{\text{mass loss of pellets at time } t}{\text{total oxygen content of iron oxides in pellets} + \text{maximum mass loss of coal}} \quad (1)$$

Results and discussion

Influencing factors on pelletizing

There are many factors influencing the properties of coal composite pellets. In this experiment, the effect of water addition and binder dosage on the quality of dried red mud-coal pellets was investigated and reasonable Pelletizing Parameters were made clear. The effect of single factor on the strength of red mud-coal composite pellets was analyzed by fixing other conditions unchanged.

Effect of water addition on compressive strength of coal composite pellets

Pelletizing moisture is different for different raw materials. Accordingly, under the condition of the molar ratio of C/O was 1:1 and the ratio of bentonite binder was 2%, the pellets were made by mixing 12%, 14%, 16%, 18%, and 20% water with red mud-coal mixture. The effect of water content on the compressive strength of red mud-coal composite pellets was analyzed and the experimental results can be seen in fig. 1.

Effect of binder dosage on dried red mud-coal pellets

Bentonite was selected as binder for coal composite pellets in the experiment. The addition of bentonite effectively improved the pelletizing property and the compressive strength

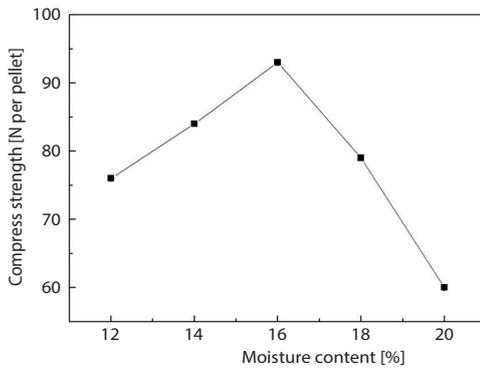


Figure 1. Water content on compressive strength of red mud-coal composite pellets

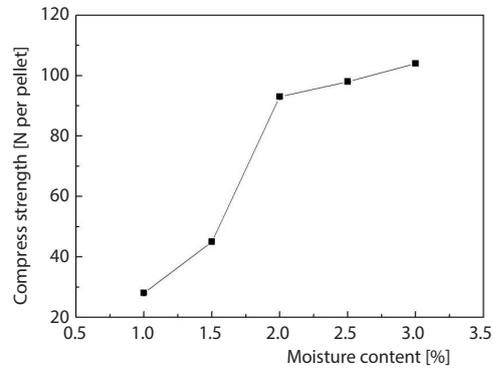


Figure 2. Bentonite content on compressive strength of red mud-coal composite pellets

of red mud-coal composite pellets. The changes of compressive strength of coal composite pellets were examined by changing the amount of bentonite. Specifically, the changes of compressive strength with bentonite content of 1.0%, 1.5%, 2.0%, 2.5%, and 3.0% were investigated in the case of 1:1 molar ratio of C/O in the mixture and 16% water content in the red mud-coal mixture. The result is shown in fig. 2.

As shown in fig. 2, when the amount of bentonite was less than 2%, the compressive strength of red mud-coal composite pellets increased obviously with the increase of bentonite content. When the amount of bentonite was more than 2%, the effect of increasing the content of bentonite on increasing the compressive strength of red mud-coal composite pellets were obvious weakened.

From the experiments, it can be seen that it is helpful to increase the compressive strength of red mud-coal composite pellets by increasing the water content of pellets and the amount of bentonite. But it also inevitably increases the energy consumption of drying process. At the same time, too much bentonite also inhibits the direct reduction, and further increases the energy consumption in reduction process. Combining all the above factors, the suitable pelletizing conditions are confirmed as 2% of the binder bentonite and 16% of the water content of red mud-coal composite pellets

Influencing factors on reduction

Effect of temperature on reduction reaction

A mixture of oxygen (O_{TFe}) and fixed carbon (C_{Fix}) in red mud-coal pellets at a mole ratio of 1:1 in nitrogen atmosphere were analyzed throughout this research. The red mud mixture is processed into pellets with a diameter of 15 mm in a disc pelletizer. Figure 3 was the curves of reduction fractions of red mud-coal composite pellets with time under reduction reaction in nitrogen atmospheres. It indicates that the rise temperature led to the increase of reduction rate, and the reduction rates increase rapidly above 900 °C.

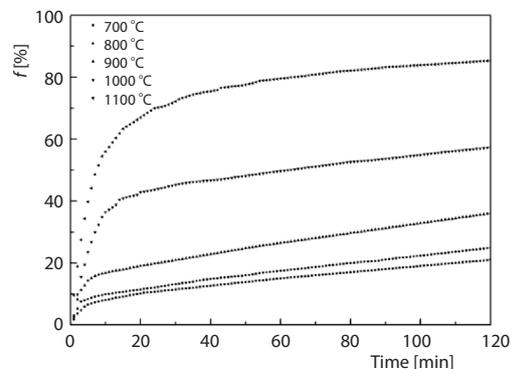


Figure 3. Effect of temperature on reduction reaction

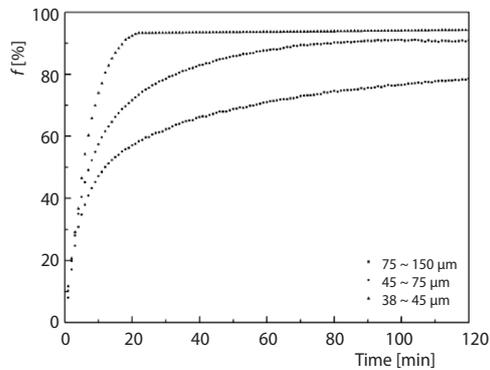


Figure 4. Effect of particle size on isothermal reduction

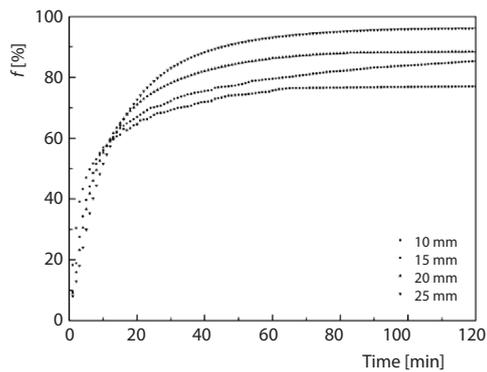


Figure 5. Effect of pellet diameter on isothermal reduction

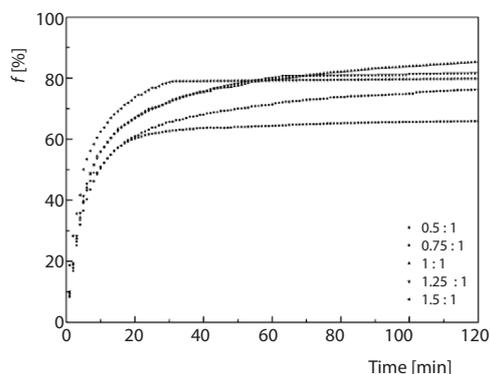


Figure 6. Effect of mole ratio on isothermal reduction

Effect of particle size on reduction reaction

A mixture of O_{TFe} and C_{Fix} in different particle size range at a mole ratio of 1:1 in nitrogen atmosphere were used throughout the study at 1100 °C. The reduction fraction for different particle size at 1100 °C was shown in fig. 4. The reduction fraction had a rapid increase at 1100 °C which showed that the reaction proceeded intensely. It was showed that different particle diameters caused different initial reaction rates. The reduction rate of red mud-coal composite pellets with the particle size range of 38-45 μm was obviously higher than the others. This may be due to the difference in specific surface area.

Effect of pellet diameter on reduction reaction

A mixture of O_{TFe} and C_{Fix} in different pellet diameter at a mole ratio of 1:1 in nitrogen atmosphere were used throughout the study at 1100 °C. The results can be showed as fig. 5. It indicated that the reduction rate decreased first and then increased as the pellets diameter increased. The decrease of reduction rate could be due to the uneven temperature in pellets at the initial phase reaction and larger specific surface area in smaller pellets. Big pellets have more abundant reaction space, the reduction rate increased as the reaction progresses.

Effect of mole ratio on reduction reaction

A mixture of C_{Fix} and O_{TFe} in red mud-coal particles at mole ratios of 0.5:1, 0.75:1, 1:1, 1.25:1, and 1.5:1 in nitrogen atmosphere were used throughout the study at 1100 °C. The results can be showed as fig. 6. It indicated that the reduction rate increased first and then decreased as the C_{Fix} and O_{TFe} mole ratios increased. The reduction at the mole ratio of 1:1 is economical. The C_{Fix} is not enough when mole ratio is less than 1:1, and the reduction rate decreased. When C/O mole ratio is more than 1:1, the pellet is in a state of excess carbon which resulting in waste of energy.

Change rule of compressive strength of reduction products

According to the previous research, reduction temperature is the very important factor affecting the reduction process of red mud-coal composite pellets. It is directly related to whether the reduction process can be realized smoothly. Therefore, the compressive strength of reductive products at 700 °C, 800 °C, 900 °C, 1000 °C, and 1100 °C was studied experimentally in the experimental conditions of C/O molar ratio 1:1, diameter 15 mm and reduction reaction time 120 minutes. The result can be seen in fig. 7.

The reduction temperature had an obvious effect on the compressive strength of the reduction products in fig. 7. The compressive strength of the red mud-coal composite pellets decreased first and then increased with the increase of temperature. The compressive strength of reductive products reached the minimum at 800 °C and 900 °C, respectively, which is basically consistent with the trend that the red mud-coal composite pellets expand first and then shrink with the increase of temperature in the reduction process.

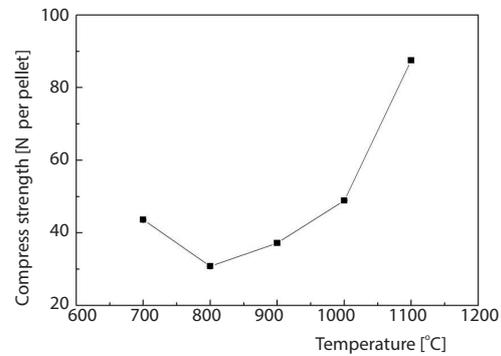


Figure 7. Reduction temperature on the compressive strength of reductive products

Iron phase transition in reduction products of red mud-coal composite pellets

The quantitative relationship between iron phase and temperature in the reduction products of red mud-coal composite pellets in the experimental conditions of C/O molar ratio 1:1, diameter 15 mm and reduction time 120 min are shown in fig. 8. Through analysis, it can be seen that the reduction of Fe^{3+} in red mud-coal composite pellets occurred below 700 °C and completed at 1000 °C basically. A small amount of Fe^{3+} still existed in the reduction product at 1100 °C. The content of Fe^{2+} in the reduction product increased at 700 °C and reached the maximum at 900 °C. With the further increase of temperature, the content of Fe^{2+} decreased. The content of metallic iron was very low below 900 °C and increased rapidly when the temperature reached above 1000 °C. The reduction product of red mud-coal composite pellets reached 80.02 % metallization rate at 1100 °C, which is consistent with the results of XRD analysis.

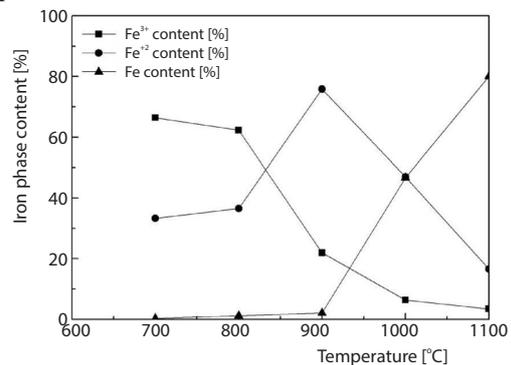


Figure 8. Relationship between iron phase of red mud-coal composite pellets and temperature

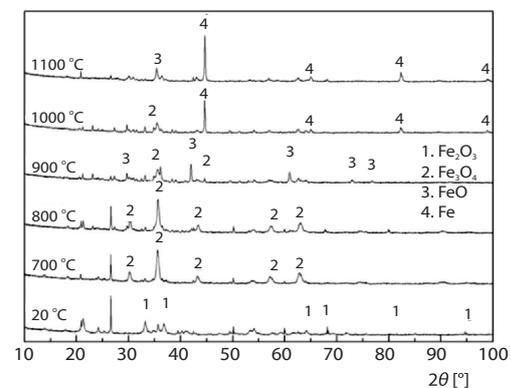


Figure 9. The XRD analysis of red mud-coal composite pellets

The X-Ray diffraction analysis

Figure 9 represents the XRD patterns of the reduced pellets at different temperatures. The transformation of iron oxides can be ob-

served from the correspondence of the peak. At 20 °C, the main phase was Fe_2O_3 . At 700 °C, Fe_3O_4 increased significantly, suggesting that the reduction reaction from Fe_2O_3 to Fe_3O_4 occurred below 700 °C. The reduction reaction from Fe_3O_4 to FeO occurred between 800 °C to 900 °C, and basically completed in 900 °C to 1000 °C. According to the characteristics of the iron oxide phase reduction, metal iron appeared at 1000 °C. At 1100 °C, metallic iron occupied the main ingredients of the sample.

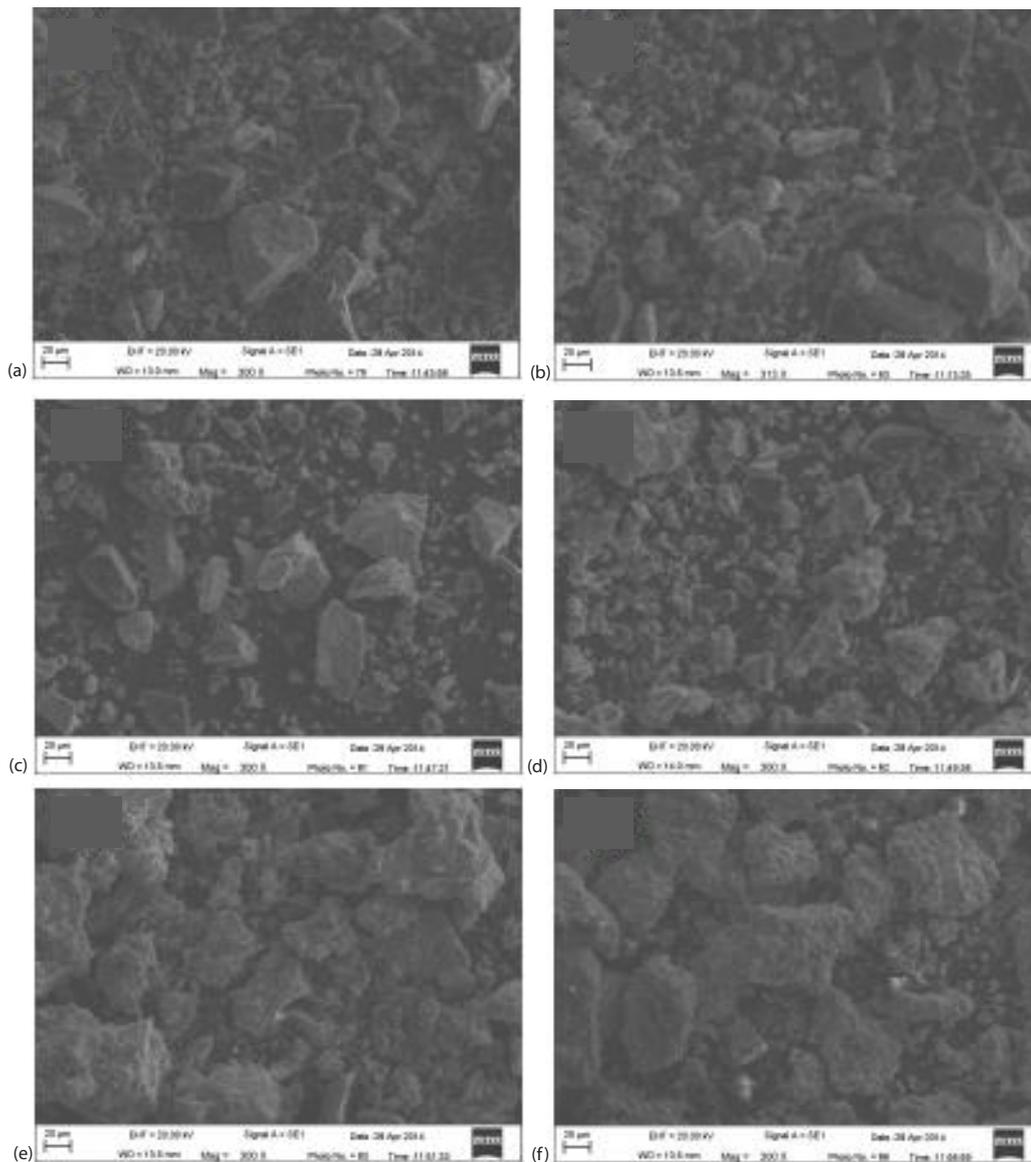


Figure 10. Microstructure analysis during isothermal reduction;
(a) 20 °C, (b) 700 °C, (c) 800 °C, (d) 900 °C, (e) 1000 °C, and (f) 1100 °C

Microstructure analysis during isothermal reduction

The microstructure change of pellets is very important to understand the characteristics of the reaction process. The red mud-coal composite pellets and heated residue at 700~1100 °C were crushed and the morphology was analyzed by scanning electron microscope. The results were shown in fig. 10. At 700 °C, the reduced samples did not show any significant change, and the structure is compact. The microscopic structure did not reveal any obvious alteration below 900 °C due to the slow reduction rate. At 900 °C, cracks and tiny pores were observed within the heated residue. The cracks and tiny pores accelerate the reduction reaction. At 1000 °C, it was showed that the particles showed clear porous structure. At 1100 °C, it was observed that there were some bright areas appeared, suggesting that the reduction degree reached a quite high level.

Conclusions

This research analyzed the direct reduction characteristics and mass loss of the red mud-coal composite pellets in different temperature, particle size, pellet diameter and mole ratio. From this current research can get the following conclusions.

- The rising temperature and decreasing particle size led to the increase of reduction rate. The reduction rate decreased first and then increased as the pellets diameter increased. The mixture of fixed C and oxygen (O_{TFe}) at a mole ratio of 1:1 is appropriate under the experimental conditions.
- Temperature plays a important role to the reduction rate. The temperature of 1100 °C is appropriate for the reduction of red mud-coal composite pellets. The reduction rate increased rapidly when the temperature reached 1100 °C.
- The reduction of Fe_2O_3 forming Fe_3O_4 occurs below 700 °C. The reduction of Fe_3O_4 forming FeO is initiated at 900 °C, the content of metallic iron was very low below 900 °C and increased rapidly when the temperature reached above 1000 °C. At 1100 °C, metallic iron occupied the main ingredients of the sample.
- At 700 °C, the reduced samples did not reveal any significant change, and the structure is compact. A few tiny pores appeared in the products at 900 °C. At 1000 °C, the appearance of the porous system prompts the reduction. At 1100 °C, some bright areas appeared which indicating that the reduction degree reached a high level.

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