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# Preparation of reduced iron powder using combined distribution of wood-charcoal by microwave heating

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ABSTRACT

In this paper, the influences of microwave heating with wood-charcoal as the reducing agent, on the reducing characterization of mill-scale were systematically investigated. The microstructures of the samples were characterized before and after microwave heating using SEM. The SEM analysis results indicated that the high-grade reduced iron powders were prepared using microwave heating. It was concluded that microwave heating technologies can be applied effectively and efficiently to the reduction process processes of iron ore concentrate.



## 1. Introduction

Iron powder with high quality is an indispensable raw material for many fields, such as powder metallurgy [1–3], magnetic materials [4], metal welding cutting, coating [5,6], wastewater treatment [7,8], medicine and food [9–11]. Its demands have been increasing stably with the booming development of auto industry.

Reduced iron powder [12,13] and atomized iron powder [14,15] are the two largest outputs at present. The processes of Sweden Höganäs Co. (the major reduced iron powder manufacturer) include two steps [16]: first, to reduce the high-purity iron ore concentrate (total iron $\geqslant$71.5%); then, the second reduction in the hydrogen gas which is processed in the belt furnace for the previous products after crush, magnetic separation and drying. During the processes, the first reduction is the key step to producing high quality iron powder. The circular crucible ring-like charging method is used – the inner and outer layers are the reduction coal, the middle layer is the iron ore concentrate, which we called the outer distribution coal. Tunnel kiln is used and heated by heavy oil, the reduction period is 53–90 h, and the total iron and metallization ratio are about 97% and 95.9%, respectively. The largest advantage of this method is that the iron ore concentrate and coal are contacted without mixing. Thus the reducing agent will not pollute the products and then the high total iron and low impurity content of reduced iron powder are assured. However, the advantage means the largest disadvantage at the same time for this method in that the non-mixing of the iron ore concentrate and coal leads to the complex reduction process, long period, energy consumption and hard-to-grind products. The reduction reaction of iron oxide of this outer distribution coal is largely influenced by the condition of mass transfer. And the conventional heating method cannot meet the energy requirement of reduction and Boudouard reaction. In addition, it leads to the products which tend to be densifying.

The characteristic of direct reduced iron (DRI) [17,18] is that the iron oxide and reducing agent are mixed completely, namely the inner distribution coal. The advantages of this method are the short production period and high metallization due to the fast speed of reduction reaction. While it also leads to both high impurity of the content of the products and low rate of total iron.

To solve the problem of long reaction period for outer distribution coal under conventional heating and the high impurity content of products for inner distribution coal, a combination of the outer and inner distribution of wood-charcoal is used in this paper

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to prepare high quality reduced iron powder in the microwave field [19–22] considering the fact that mill-scale, coal and wood-charcoal all have a good property of microwave absorbing.

## 2. Experimental

### 2.1. Materials

The compositions of the mill-scale and wood-charcoal are shown in the following Tables 1 and 2, respectively. The particle size distribution of the material and wood-charcoal used is represented in Fig. 1. All these materials are milled by the ball grinding mill. The percentages shown in full paper are weight percentages.

### 2.2. Methods

A self-made microwave tube furnace, which utilizes a single-mode continuous controllable power is utilized for all experiments and shown in Fig. 2. The microwave frequency is 2.45 GHz, while the output power is controlled within the maximum of 1500 W. The activation temperature is controlled by varying the input microwave power. The activation temperature is measured by nickel chrome–nickel silicon armor type thermocouple which is in contact with the material. The thermocouple has dimension of length of 1000 mm, 3 mm diameter, with the temperature range of 0–1250 °C, and a measurement precision of ±0.5 °C.

Distribution: the materials are divided into three layers. At the bottom layer is the mixture of wood-charcoal and calcium carbonate, and at the mid-layer is the mixture of wood-charcoal and mill-scale while at the upper layer is wood-charcoal.

Note: $a$, $b$, $c$ and $d$ denote the mass of the corresponding materials in Fig. 3. Wood-charcoal at the mid layer is called inner distribution wood-charcoal and can be defined as:

$$\text{inner distribution wood} - \text{charcoal} = \frac{b}{a+b} \times 100\% \quad (1)$$

Wood-charcoal at the bottom is named as outer distribution wood-charcoal and can be defined as:

$$\text{outer distribution wood} - \text{charcoal} = \frac{b+c}{a+b+c} \times 100\% - \frac{b}{a+b} * 100\% \quad (2)$$

Combined distribution of wood-charcoal means the combination of the inner distribution wood-charcoal and outer distribution wood-charcoal. If $c = 0$ g, $d = 0$ g and the reductant is carbon, the stoichiometric content of reductant required for reduced completely of mill-scale is 15.78% [20].

### 2.3. Design of experiments

Experiment Process: Charge as Fig. 2. Subsequently, pass $N_2$ for 30 min, start the microwave, stop passing $N_2$. Then start the experiment according to the process.

Experiment 1: $a = 27$ g, $b = 3$ g, $c = 3.75$ g, $d = 2.5$ g. Namely, both the percentages of the inner distribution wood-charcoal and the outer distribution wood-charcoal are 10%. The gas released at 550 °C, 850 °C, 950 °C, and 1150 °C was collected by displacement of water and the gas composition was analyzed by gas chromatography. The reduction temperature was set at 1150 °C and the holding time were 5 min and 50 min, respectively. Then the products were examined by SEM, and the total iron and metallization ratio of the sample reduced by 50 min were measured.

Experiment 2: $a = 0$ g, $b = 30$ g, $c = 0$ g, $d = 0$ g. This means that the material used in this experiment is only the reduced agent, wood-charcoal. The components of the gas released by wood-charcoal during the heating process were collected and measured.

$$\text{total iron} = \frac{M_1}{M_0} \times 100\% \quad (3)$$

$$\text{metallization ratio} = \frac{M_2}{M_1} \times 100\% \quad (4)$$

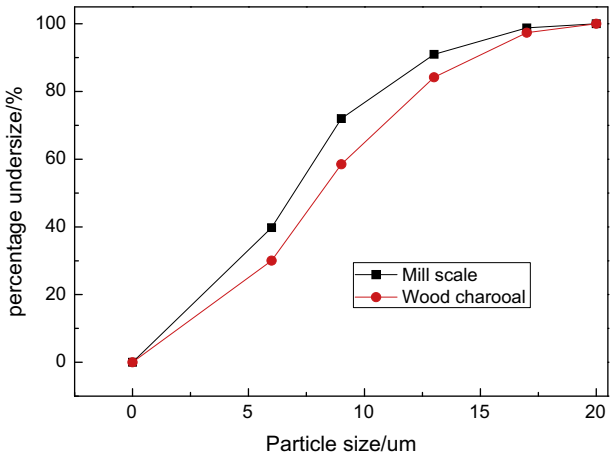


**Fig. 1.** Particle size distributions of mill-scale and wood-charcoal.

$M_0$ is the mass of a sample, $M_1$ is the mass of Fe, $M_2$ is the mass of zero valent iron. Determination of total iron and metallization ratio is measured using potassium dichromate: Redox indicators.

## 3. Results and discussion

The total iron of the reduced iron powder obtained (with a holding time 50 min at 1150 °C) in experiment 1 was 98.56%, and the metallization ratio was 99.25%. Based on the analysis of XRF (Shimadzu, XRF-1800 Sequential WDXRF), the detailed composition of iron powder is listed in Table 3. From the table, it can be seen that the chemical composition of the reduced iron powder meets the specification of the HY100.23 first-class iron powder standard.

Fig. 4 shows the gas composition produced by wood-charcoal at different temperature under microwave heating in experiment 2. Fig. 5 shows the off-gas composition produced at different temperature in the microwave field under the condition that the ratio of both the inner and outer distribution wood-charcoal is 10% in experiment 1.

Fig. 6 is the SEM of the mixed raw material with 10% of wood-charcoal. Wood-charcoal corresponds to the darker color, with smooth surface and clear profile, while the rest of the portion corresponds to the mill-scale.

Figs. 7 and 8 are the SEM of the reduced iron powder with an inner distribution wood-charcoal of 10%, outer distribution wood-charcoal of 10%, and reduction temperature of 1150 °C. But the holding time is 5 min and 50 min, respectively.

The reduced iron powder was prepared in microwave field by combined distribution of wood-charcoal with the holding time 50 min (using Höganäs process-ring-like charging method, heavy oil was used as fuel and the reduction period was 172 h). The chemical composition of the products meets the HY100.23 first-class iron powder standard. There are four reasons accounting for this.

**Table 1**
Compositions of mill-scale (total iron 74.25%) (%).

| FeO | $Fe_2O_3$ | $Fe_3O_4$ | $SiO_2$ | MnO | P | S | CuO | $SnO_2$ | CaO | $Cr_2O_3$ |
|---|---|---|---|---|---|---|---|---|---|---|
| 61.31 | 36.36 | 1.61 | 0.096 | 0.30 | 0.014 | 0.017 | 0.12 | 0.09 | 0.032 | 0.029 |

**Table 2**
Compositions of wood-charcoal (%).

| Fixed carbon | Volatile organic matter | $H_2O$ | CaO | FeO | MgO | S | $K_2O$ | $Na_2O$ |
|---|---|---|---|---|---|---|---|---|
| 72.58 | 22.26 | 4.67 | 0.40 | 0.01 | 0.014 | 0.0028 | 0.069 | 0.0005 |

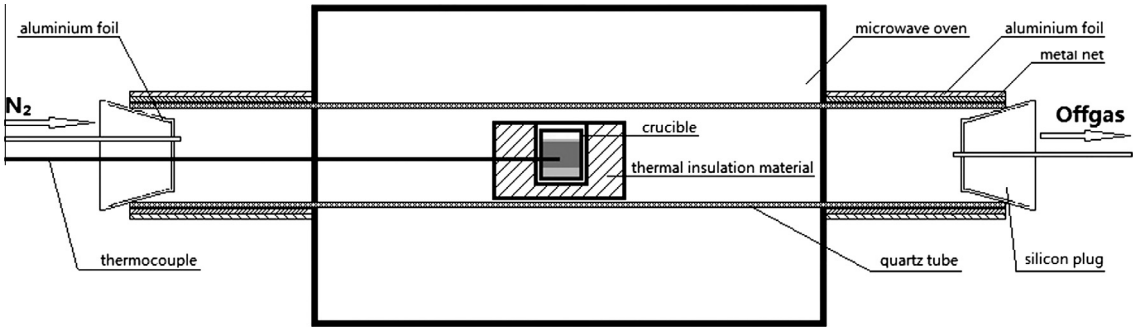


**Fig. 2.** Diagram of microwave tube furnace.

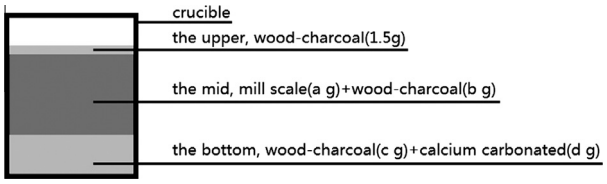


**Fig. 3.** Diagram of crucible filling.

Firstly, the iron scale is pure and the ash content of wood-charcoal is very low, which provide the prerequisites for producing high purity iron powder.

Secondly, the inner distribution wood-charcoal is 10%, which is far below the theoretic content 15.8%. It ensures that the wood-charcoal reacts completely and few ash content of wood-charcoal remains in the products. The well contact between wood-charcoal and iron powder makes the latter reduced easier to reduce (as is shown in Fig. 6). Besides, as the wood-charcoal is consumed, there remains a large space which will improve the condition of mass transfer for the internal gas of raw material (As is shown in Fig. 7). The high volatility of wood-charcoal also improves its reducibility.

Thirdly, there are 10% of wood-charcoal and moderate content of $CaCO_3$ in the bottom. The reducing gas produced in the process will further reduce the non-reduced iron oxide in the middle layer. In this way, the high metallization ratio of iron scale and the total iron of iron powder can be assured.

Fourthly, the microwave heating ensures the energy supply for the reaction in the crucible, which overcomes the limitation of heat transfer by traditional heating methods.

The reduction mechanism of producing reduced iron powder by combined distribution of wood-charcoal is as follows:

Firstly, at the initial stage of the microwave heating, because of the existence of air among the powder, reactions (5) and (6) take place and produces CO and $CO_2$. When the temperature rises up, the charcoal's volatile organic matter volatilizes and decomposes, producing $H_2$ and $CH_4$, etc. Iron oxide is reduced preliminarily by CO and $H_2$, as depicted by chemical Eqs. (9) and (10).

Secondly, along with the temperature increasing, direct reduction takes place at the part where mill-scale and inner distribution wood-charcoal contact as depicted by Eq. (8).

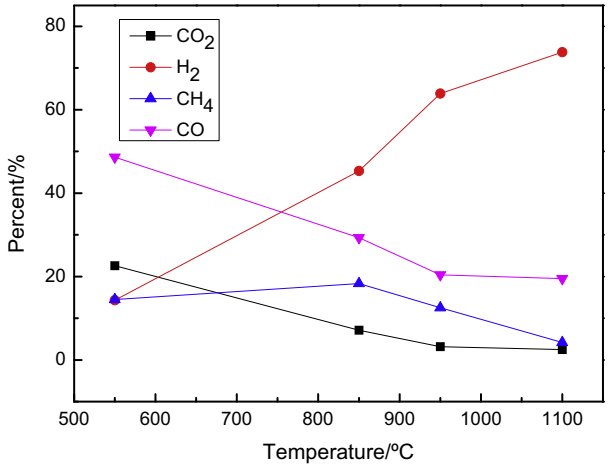


**Fig. 4.** Gas compositions of wood-charcoal by microwave heating (volume percent).

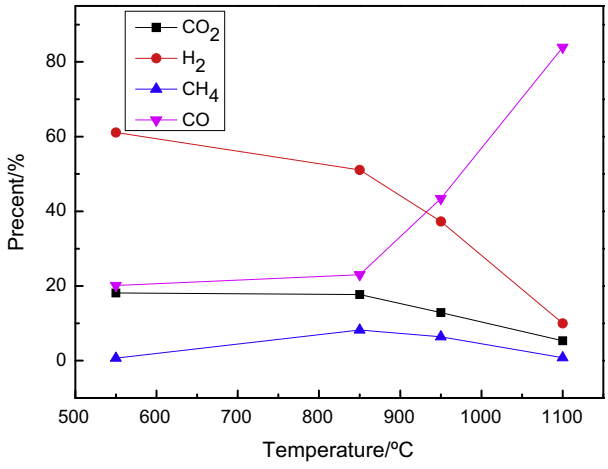


**Fig. 5.** Gas compositions of combination distribution of wood-charcoal by microwave heating (volume percent).

**Table 3**
Composition of reduced iron powders (%).

| Fe | Si | Mn | P | S | Cu | Mg | Sn | Ca | Cr |
|---|---|---|---|---|---|---|---|---|---|
| 99.16 | 0.0584 | 0.3094 | 0.0129 | 0.0153 | 0.127 | 0.1253 | 0.0847 | 0.073 | 0.0245 |

*Note:* XRF is not able to recognize light symbols such as O.

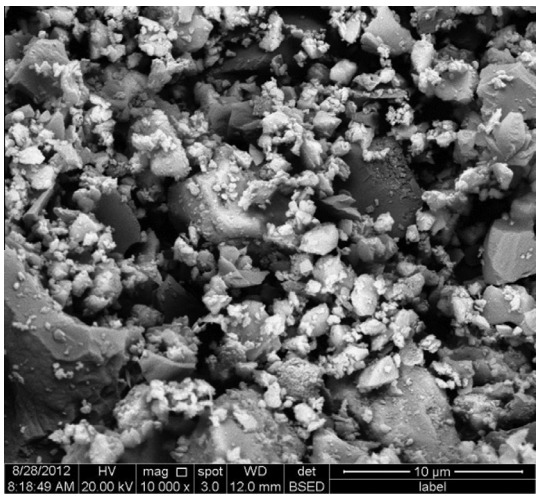


**Fig. 6.** SEM of the mixture of wood-charcoal and mill-scale.

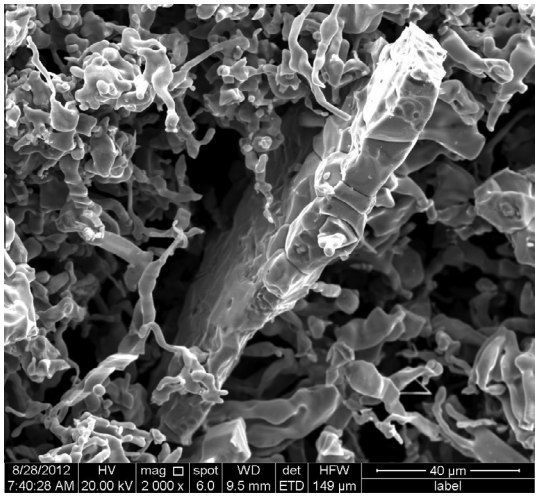


**Fig. 7.** SEM of reduced iron powder of 5 min for holding time at 1150 °C.

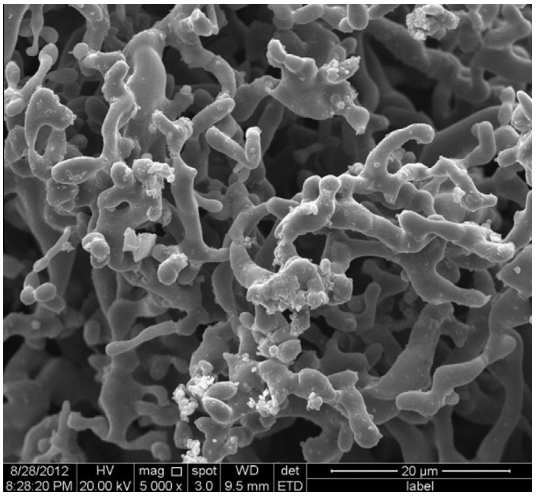


**Fig. 8.** SEM of reduced iron powder of 50 min for holding time at 1150 °C.

Thirdly, as can be seen from Figs. 6 and 7, the mill-scale and charcoal only contact with each other partly. Direct reduction of mill-scale will stop when it is reduced to some extent. At this time, the reduction of mill-scale will be dominated by indirect reduction (Eq. (9)), whose process is controlled by Boudouard reaction (Eq. (7)).

Fourthly, $CO_2$ is produced from the decomposition of calcium carbonate at the bottom. Then $CO_2$ reacts with charcoal and produces CO (Eqs. (11) and (7)). CO further reduces mill-scale during the rising process.

The results of the reduction: at the bottom layer, the calcium carbonate and charcoal are consumed largely. At the middle layer, the oxygen atom of mill-scale is nearly taken away completely. The wood-charcoal is consumed completely except its ash content. The reduced iron particles are cohered each other and form a spongy-net-like structure (see Fig. 8). At the top layer, the charcoal acts as a barrier to prevent the oxygen outside the crucible from entering in and to be consumed partly.

$$2C + O_2 = CO \quad (5)$$

$$C + O_2 = CO_2 \quad (6)$$

$$C + CO_2 = 2CO \quad (7)$$

$$Fe_xO_y + yC = xFe + yCO \quad (8)$$

$$Fe_xO_y + yCO = xFe + yCO_2 \quad (9)$$

$$Fe_xO_y + yH_2 = xFe + yH_2O \quad (10)$$

$$CaCO_3 = CaO + CO_2 \quad (11)$$

## 4. Conclusion

This study presents the research results of preparation process of reducing product, high-grade reduced iron powders from mill-scale with wood-charcoal as the reducing agent by carbothermal reduction using microwave heating. And its microstructure of the samples was characterized before and after microwave treatment using SEM. Reduced iron powder with a total iron of 98.56%, a metallization ratio of 99.25% and a chemical composition meeting "the specification of the HY100.23 first-class iron powder standard" can be obtained by microwave heating with wood-charcoal as the reducing agent, the reduction temperature at 1150 °C and a holding time 50 min through the combined distribution of wood-charcoal. Based on the results, this method can be applied effectively and efficiently way for the reduction process processes of iron ore concentrate.

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