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Iron ore reduction in a small fluidized bed

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Abstract – To optimize the process and improve the degree of reduction, a two-stage experiment was designed. It was carried out in a micro-fluidized bed. It is operated as a differential reactor to ensure every particle in the micro-fluidized bed is at equal temperature, concentration and residence time. The experiment used iron ore powder from Yangdi. The reducing gas and temperature in the pre-reduction stage were, respectively, pure CO and 625 °C. In the final reduction stage, the temperature and reducing gas were, respectively, 800 °C and pure CO. The residence time was between 10 min and 60 min. In addition to the experiment, a microscopic technique was also carried out. The test shows a significant influence of the temperature and residence time of the two-step experiment on the final reduction degree.

To compensate for the shortage of high-quality steel scrap, direct reduced iron (DRI) has become an important industrial material in steel plants.

Direct reduced iron (DRI) is produced by an industrial fluidized bed (in the FIOR, FINMET and FINEX processes). It requires high-quality material of iron ore with large porosity, large surface area, uniform particle size, etc. So, the degree of reduction is very much influenced by the initial conditions of the iron, and is usually relatively low. Our experiment was carried out to improve the initial conditions of iron ore powder and acquire a higher degree of reduction.

Comparing the traditional experiments with a fluidized bed, the most commonly used equipment is a circulating fluidized bed [1], large-sized fluidized bed, etc. These instruments are integral reactors. Various parts of the reactor volume are at different temperatures and gas concentration. A temperature and concentration gradient occurs over the whole bed. Therefore, this experiment used a micro-fluidized bed.

A two-stage experiment was designed in a micro-fluidized bed. The first stage is pre-reduction. The purpose of this stage is to obtain some surface morphology. The second stage is the final reduction. The products resulting from the pre-reduction stage were used as reactants in the final reduction stage. The influence of the two-step experiment on the degree of reduction while the reactant particles acquired some surface morphology was studied.

1 Experimental

1.1 Experimental setup

To investigate the influence of the two-step experiment on the reduction degree, a micro-fluidized bed [2–5] was used. The operating conditions are as follows:

(1) the working pressure in the micro-fluidized bed reactor is normal pressure;
(2) reducing gas is pure CO;
(3) operating time is between 10 and 60 min;
(4) operating temperature is below 800 °C;
(5) the material is Yangdi iron ores and the size of the particles is 150 microns.

The micro-fluidized bed is a differential operating reactor. This is the basic rule of the perfectly mixed fluidized bed reactor: all

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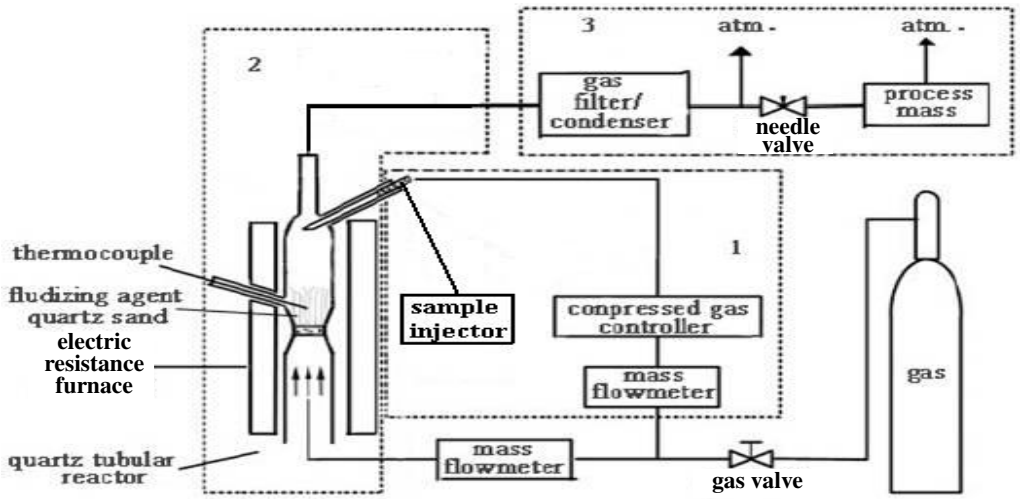


Fig. 1. Basic principle of experimental setup.

particles have similar residence time, temperature and pressure. The basic principle of the experimental setup is shown in Figure 1.

Fluidizing agents and iron ore were, respectively, placed in the reactor and sample injector. The inert gas flowing through the reactor prevented the iron ore from reacting with other materials in the air during the preheating phase. After reaching the desired process temperature, the inert gas was switched to reducing gas. When the concentration of CO remained steady, iron ore were shot into the reactor by sample injector and reacted with the CO gas. After the required reduction time, the reducing gas was switched back to inert gas to prevent reoxidation. When the temperature of the reactor cooled down to room temperature, the reduced iron ore samples were removed from the reactor and part of them were analyzed by a titrimetric method (iron chloride method) for overall Fe_{tot}, Fe^0 and Fe^{2+} [6,7]. The steps above are the pre-reduction stage.

The rest of the reduced iron ore samples were used to repeat the above steps in conditions of final reduction. That is the final reduction stage.

To obtain knowledge about the changes in the particles' surface, the microscopic morphology of the raw material and reduced iron ore particles were investigated in reflected light on a SEM (EVO 18 Special Edition, Carl Zeiss NTS).

1.2 Reduction tests

To investigate the influence of the two-step experiment on the reduction degree, the experiment was divided into two parts. The first part of the experiment studied the influence of pre-reduction conditions on the reduction degree; the experimental conditions are shown in Table 2. As can be seen in Table 2, the experiments had different pre-reduction conditions and the same final reduction conditions. The pre-reduction temperature was between 625 °C and 680 °C. The pre-reduction time was 10 min and the reducing gas pure CO. The second part of the experiment studied the influence of final reduction conditions on the reduction degree; the experimental conditions are shown in Table 4. As can be seen in Table 4, the experiments had the same pre-reduction conditions and different final reduction conditions. The temperature, reduction time and reducing gas in the pre-reduction stage were, respectively, 625 °C, 10 min and pure CO. In the final reduction stage, temperature was between 400 °C and 800 °C, reduction time was from 10 min to 60 min and the reducing gas was also pure CO.

The experiment used Yangdi iron ores with a size of 150 microns. The chemical composition of the Yangdi iron ores is shown in Table 1. The temperature, mass flow, reaction time and variation of oxygen in the two-step experiment were recorded by computer.

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Table 1. Chemical composition of Yangdi iron ores (mass percent, %).

TFe	FeO	SiO_2	CaO	Al_2O_3	MgO	S	P
57.8	0.3	5.418	0.16	1.32	0.08	0.016	0.008

Table 2. Operating conditions of the experiment.

	Pre-reduction stage					Final reduction stage
T/°C	625	650	660	670	680	800
t/min	10					20
Reaction gas	pure CO					pure CO

The two-step experiment is different from the traditional experiment. The most commonly used equipment of the traditional experiment is a large-scale fluidized bed. This instrument is an integral reactor. For the decrease in particle intensity and the change in the heat transfer mode along the reactor height direction, various parts in the reactor have different temperatures and concentrations. However, the two-step experiment used a differential reactor. It could ensure the temperature and concentration in the reactor being constant. Therefore, the experiment carries out some exploratory research.

1.3 Determination of degree of reduction

Let the total reduction degree of iron ore powder in a micro-fluidized bed be R_T.

$$R_T = R_P + R_F \tag{1}$$

where R_P = the degree of reduction in the pre-reduction stage;
R_F = the degree of reduction in the final reduction stage.

The pre-reduction degree (R_P) is as defined by:

$$R_P = \frac{O_P}{O_T} \tag{2}$$

where O_P = weight loss of oxygen of iron oxide in the pre-reduction stage;
O_T = total weight of oxygen initially contained in the iron oxide of the ore.

Then the products resulting from the pre-reduction stage were used as reactants in the final reduction stage. So, the final reduction degree (R_F) is calculated by equation (3):

$$R_F = \frac{O_F}{O_T} \tag{3}$$

where O_F = weight loss of oxygen of iron oxide in the final reduction stage;
O_T = total weight of oxygen initially contained in the iron oxide of the ore.

2 Results and discussion

2.1 The variation of temperature in the pre-reduction stage

The curve trace of total reduction degree versus temperature of pre-reduction is shown in Figure 2. The reduction degree in the pre-reduction stage increases with increasing pre-reduction temperature. The apparent morphology of the Yangdi ore particles after the pre-reduction stage is shown in Figure 3a. When the pre-reduction temperature is between 625 °C and 680 °C, the apparent morphology forming on the surface of the Yangdi iron ore does not show a great change, and so the apparent morphology after the pre-reduction stage can be replaced with the apparent morphology under the condition of 625 °C. The result is shown in Figure 3a.

As can be seen in Figure 3a, the material forming on the surface of the Yangdi particles is a mixture of porous wustite and metallic iron. According to the inference of Figure 2 above, the proportion of metallic iron in the mixture forming on the surface of the particles of Yangdi iron ore increases with increasing pre-reduction temperature, and the proportion of porous wustite in the mixture decreases with it.

Yangdi iron ores after the pre-reduction stage were used as reactants for the final reduction stage and in the same final reduction conditions. Under these conditions, the chemical reaction rate was relatively high,

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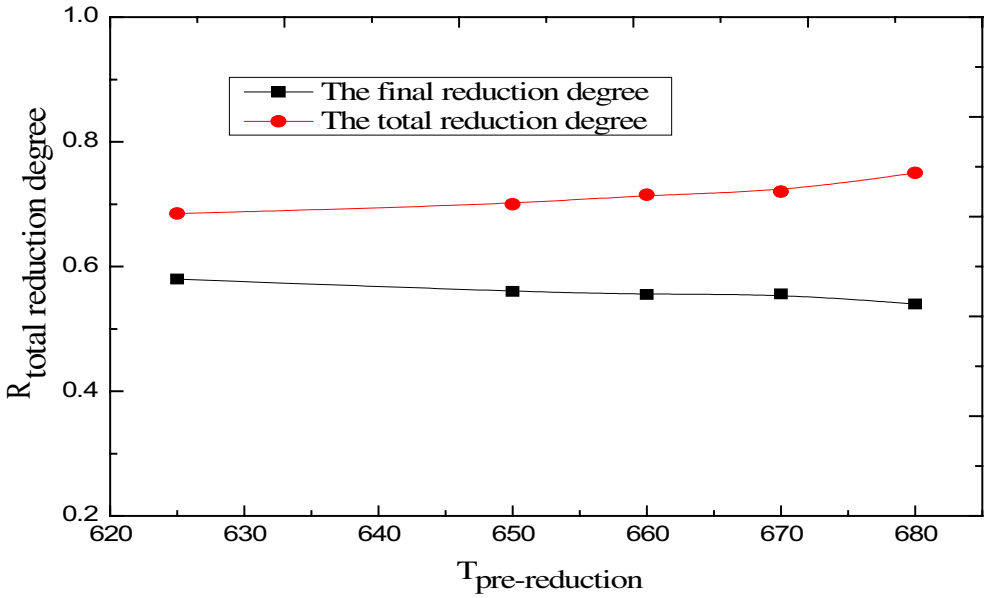


Fig. 2. Reduction degree versus pre-reduction temperature.

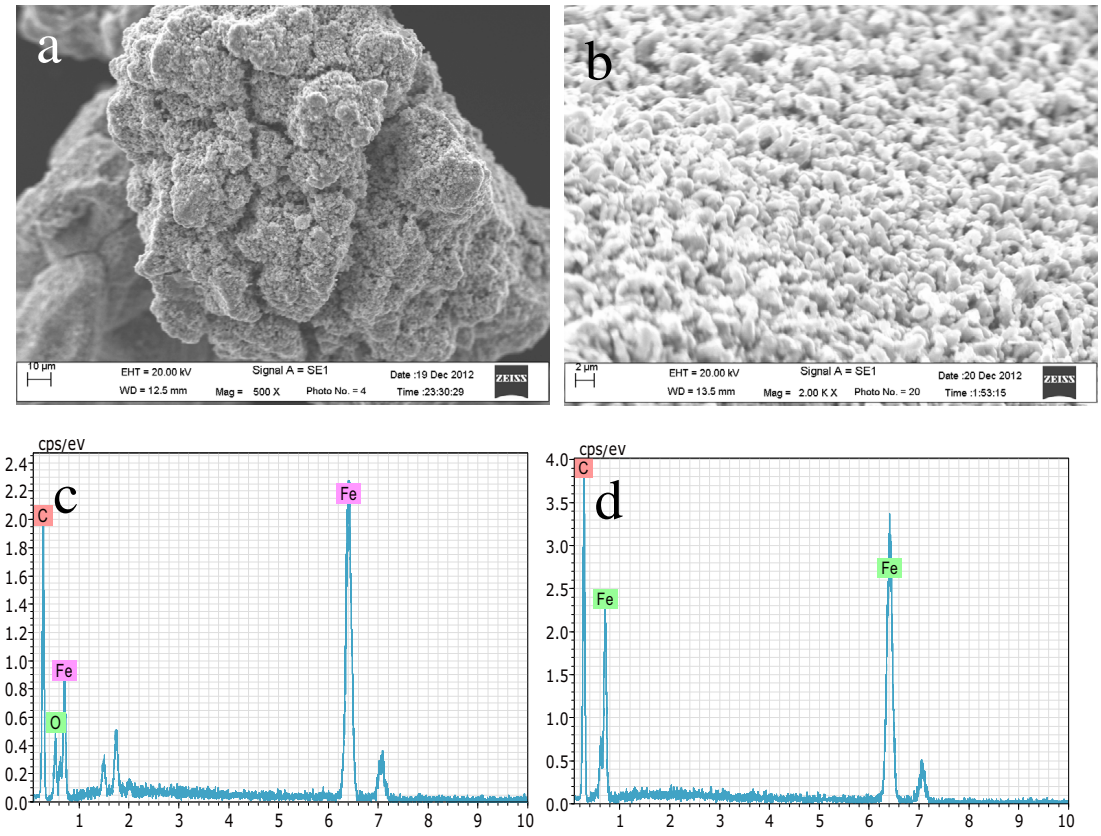


Fig. 3. Reduced ores and SEM energy spectra after the pre-reduction stage and after the final reduction stage.

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Table 3. The comparison of the two-step experiment and traditional experiment.

	Two-step experiment					Traditional experiment
Reduction temperature/°C	625	650	660	670	680	800
Reduction time/min	10 (Pre-reduction time) + 20(Final reduction time)					30 min
Total reduction degree/%	0.685	0.7	0.715	0.72	0.75	0.48

because the temperature in the final reduction stage was 800 °C and the specific surface area of the particles of Yangdi iron ore after the pre-reduction stage increased a lot compared with undressed ore. At this moment, the porous wustite forming on the surface of the Yangdi particles after the pre-reduction stage was reduced to metallic iron. The metallic iron appeared in large amounts and bonded with itself. It made the surface of the Yangdi particles form a dense metallic layer and blocked the pores of the particle surface. The porosity of the Yangdi iron ore gradually decreased with the chemical reaction happening. When the porosity forming on the surface of the Yangdi iron ore was equal to zero, the chemical reaction ended. The results are shown in Figures 3a–3d. The pictures c and d are, respectively, the SEM energy spectra of a and d.

However, there was only a different temperature in the pre-reduction stage; the other conditions were the same. So, the chemical reaction rate increased with increasing temperature in the pre-reduction stage. There was more porous wustite which was reduced to metallic iron on the surface of the Yangdi particles. The porosity gradually decreased with increasing temperature in the pre-reduction stage. Therefore, under the same final reduction conditions, it only required less oxygen loss (FeO → Fe) to form a dense metallic layer on the surface of the Yangdi particles. The dense metallic layer prevented reducing gas from diffusing into the Yangdi particles and the chemical reaction ended. Therefore, the total reduction degree decreased with increasing temperature in the pre-reduction stage.

The mixture of porous wustite and metallic iron formed on the surface of the Yangdi particles under temperatures from 625 °C to 680 °C in 10 min in the pre-reduction stage. The surface morphology could not prevent reducing gas from diffusing into the Yangdi particles and reacting with the iron oxide because of the porous wustite. Therefore, the chemical reaction rate increased with increasing pre-reduction temperature. According to the unreacted shrinking core model [8], the reduction depth along the radius direction of particles increased with increasing pre-reduction temperature. When the particles of the Yangdi powder were under the final reduction conditions, the particle surface was reduced to metallic iron until the surface porosity was equal to zero. For the particles of Yangdi iron ore, the deeper the depth along the radius direction of the particle, the greater the total reduction degree. This tallied with the experimental results.

2.2 Comparison of reduction degree

The results of the two-step experiment and traditional experiment are as shown in Table 3. The traditional experiment used similar reaction conditions, as shown in Table 3. The pre-reduction time plus the final reduction time in the two-step experiment equals the time of the traditional experiment. As can be seen in Table 3, the total reduction degree of the two-step experiment is greater than the reduction degree of the traditional experiment. The maximum value of the total reduction degree in the two-step experiment increased by 27% compared with the reduction degree in the traditional experiment. Therefore, the two-step method is more beneficial for enhancement of the reduction degree.

2.3 The variation of temperature in the final reduction stage

The experiment studied the influence of the final reduction conditions on the reduction

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Table 4. Operating conditions of the experiment.

	Pre-reduction stage	Final reduction stage									
T/°C	625	400	450	500	550	600	625	650	700	750	800
t/min	10 min	10, 20, 30, 40, 50, 60 min									
Reaction gas	pure CO	pure CO									

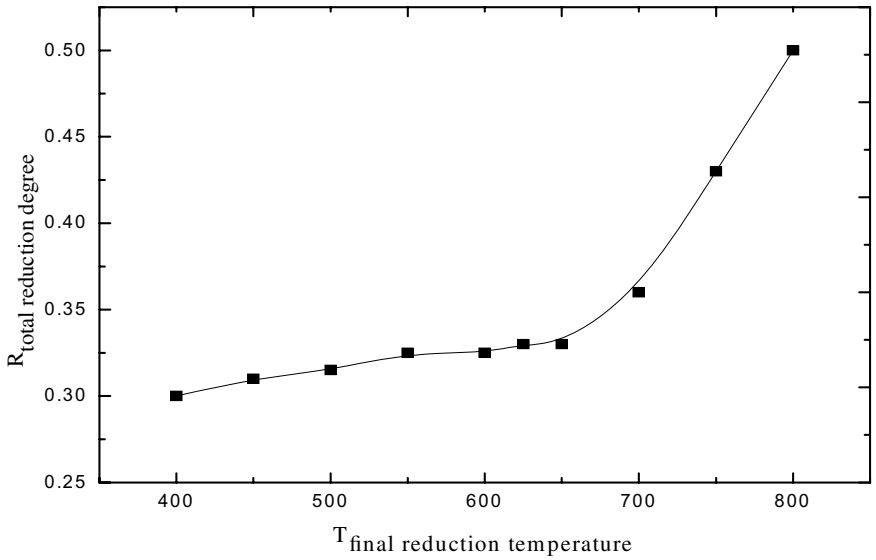


Fig. 4. The total reduction degree versus the final reduction temperature.

degree under the conditions of porous surface morphology. Therefore, 625 °C was chosen for the pre-reduction temperature, because the proportion of porous wustite on the particle surface is the highest, along with porosity, at 625 °C. The operating conditions of the experiment are shown in Table 4.

The curve trace of the total reduction degree versus the temperature of final reduction is shown in Figure 4.

When the temperature of the final reduction stage was less than 650 °C, the total reduction degree increased slowly with increasing temperature in the final reduction stage.

When the temperature in the pre-reduction stage was at 625 °C, the particles of Yangdi iron ore were reacted with pure CO. A mixture of porous wustite and metallic iron formed on the surface of the Yangdi particles under these conditions. The interior of the Yangdi particles is unreacted hematite and some magnetite produced by CO. According to the unreacted shrinking core model, the order from the inside out was hematite, magnetite and wustite. Most of the particle surface was wustite because the temperature and residence time in the pre-reduction stage are, respectively, high and long. The products produced by the pre-reduction stage were used as reactants in the final reduction stage. When reactants were in the final reduction conditions (temperature was less than 650 °C), the reaction from wustite to metallic iron seldom happened. The reaction from hematite to magnetite and from magnetite to wustite was the main reaction. The reducing gas diffused into the interior of the Yangdi particles and reacted with hematite or magnetite. The results are shown in Figure 3a. All reactions had the same pre-reduction degree because of the same pre-reduction conditions. Therefore, the total reduction degree increased slowly with increasing final reduction temperature.

According to the unreacted shrinking core model, the surface of reactants in the final reduction stage became less compared with reactants in the pre-reduction stage, because in the final reduction stage, the reaction from hematite to magnetite and from magnetite to wustite was the main reaction when the temperature was less than 650 °C, and the reaction interface moved to

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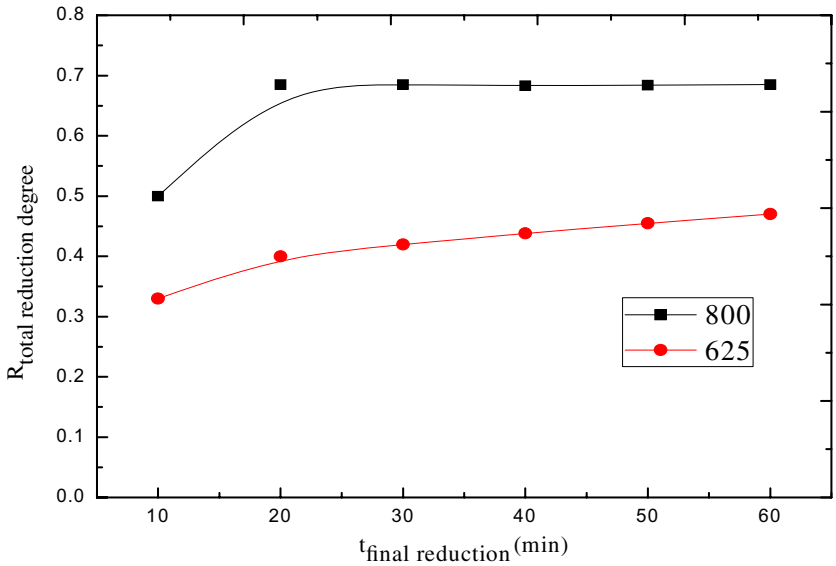


Fig. 5. The total reduction degree versus final reduction time.

the interior of the Yangdi particles. Therefore, the chemical reaction rate in the final reduction stage was slow but increased with increasing final reduction temperature.

Therefore, the total reduction degree slowly increased with increasing final reduction temperature when the final reduction temperature was less than 650 °C.

When the temperature in the final reduction stage was higher than 650 °C, the total reduction degree sharply increased with increasing final reduction temperature. Firstly, the temperature in the final reduction stage was relatively high and benefited the reaction from wustite to metallic iron. Secondly, the main material on the surface of the Yangdi iron ore was wustite. Finally, the surface area of the Yangdi iron ore in the final reduction stage grew rapidly compared with the original ore. The three aspects above sharply increased the chemical reaction rate.

Therefore, the total reduction degree sharply increased with increasing final reduction temperature when the final reduction temperature was higher than 650 °C.

2.4 The variation of residence time in the final reduction stage

The operating conditions of the experiment are shown in Table 4; the residence time in the final reduction stage was varied from 10 min to 60 min.

As can be seen in Figure 4, the total reduction experiments were, respectively, carried out in the temperature ranges of 400 °C to 650 °C and 650 °C to 800 °C to investigate the influence of the final reduction time on the total reduction degree. The points of 625 °C and 800 °C were chosen as the temperature points of the reduction time experiments in the final reduction stage. The results are shown in Figure 5.

When the temperature in the final reduction stage is at 625 °C, the total reduction degree increased with increasing residence time in the final reduction stage, but the rising slope of the total reduction degree gradually decreased. The Yangdi iron particles had a certain surface morphology which consisted of porous wustite and metallic iron from the pre-reduction stage. The porous surface morphology did not prevent reducing gas from continuing to diffuse into the interior of the Yangdi particles. When the products of the pre-reduction stage were used as reactants in the final reduction stage, the reduction reaction continued to happen. At this moment, the reaction interface gradually moved into the interior of the Yangdi particles as the residence time in the final reduction stage increased. According to the unreacted shrinking core model, the surface

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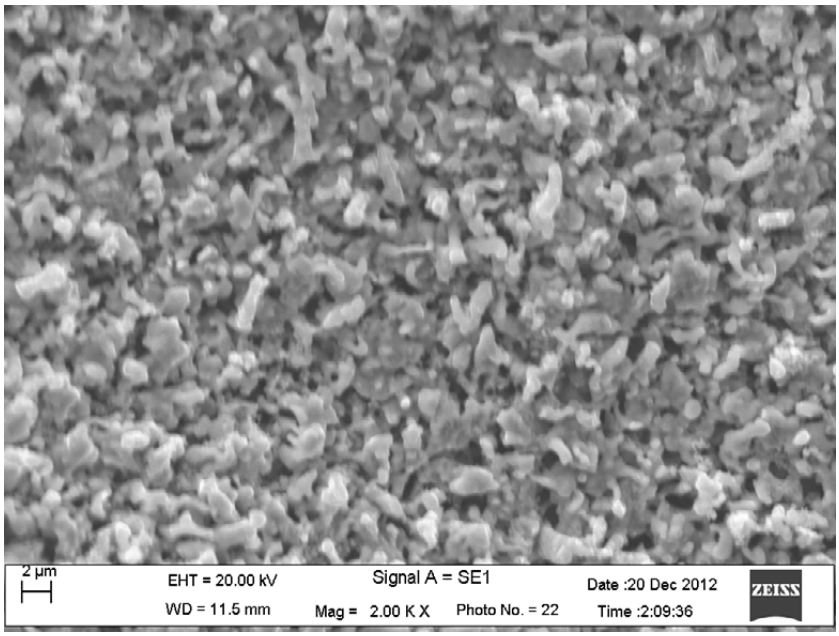


Fig. 6. The reduced ore after the final reduction stage.

area of the reduction reaction gradually decreased with increasing residence time in the final reduction stage. It led to a decrease in the interface rate. Therefore, the rising slope of the total reduction degree gradually decreased with increasing residence time in the final reduction stage.

When the temperature was at 800 °C and the residence time was less than 20 min in the final reduction stage, the total reduction degree increased sharply with increasing residence time. Under the final reduction conditions, the reaction from wustite to metallic iron kept on happening with increasing residence time of the final reduction stage. The amount of metallic iron sharply increased, and thus the total reduction degree too. However, when the residence time of the final reduction stage was longer than 20 min, the total reduction degree did not change greatly with increasing reduction time. The Yangdi powder after the pre-reduction stage was under final reduction conditions, and the porous wustite on the surface of the Yangdi powder was reduced to metallic iron. Under the final reduction conditions, the chemical reaction rate was fast because the temperature of the final reduction was higher and the surface area of the Yangdi powder was larger. A lot of metallic iron formed on the surface of the Yangdi powder. When the residence time of the final reduction was longer than 20 min, the metallic iron bonded with itself and formed a dense layer. The dense layer (Fig. 6) prevented reducing gas from continuing to diffuse into the interior of the particles. At this moment, the reaction ended. Therefore, the total reduction degree did not change greatly when the residence time of the final reduction was longer than 20 min.

3 Conclusions

(1) The two-step experiment greatly increases the reduction degree compared with the traditional experiment. The maximum value of the reduction degree of the two-step experiment increased by 27% compared with the traditional experiment when the pre-reduction temperature was at 680 °C.
(2) Pre-reduction has a significant effect on the total reduction degree when the pre-reduction temperature is between 625 °C and 680 °C. A mixture of porous wustite and metallic iron is formed on the surface of the Yangdi particles. It increases the surface area of the Yangdi powder. It finally changes the morphology of the particles and is beneficial for increasing the total reduction degree.

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(3) The final reduction temperature also has an important influence on the total reduction degree. When the surface of the Yangdi particles acquires the structure of porous wustite and metallic iron, the influence of the final reduction temperature on the total reduction degree is not always the same. When the final reduction temperature is less than 650 °C, the total reduction degree increases slowly with increasing final reduction temperature. However, when the final reduction temperature is higher than 650 °C, the total reduction degree increases sharply.

(4) Under the same pre-reduction temperature and different final reduction conditions, there is a slowing down of the kinetics of reduction at 800 °C, due to the dense layer of Fe on the surface of the grains.

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