Pig Iron Making by Focused Microwave Beams with 20 kW at 2.45 GHz

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(Received on April 8, 2012; accepted on August 16, 2012)

The furnace with maximum 20 kW was constructed using focused 8 microwave beams at 2.455 GHz into the center of applicator (electromagnetic load chamber) to make high density electromagnetic field. By heating with the power of 17.5 kW during over 35 min, pig iron has been effectively produced from 1 kg of the mixed powder of magnetite ore and 18 mass% graphite. When wustite was reduced to iron, luminescence was emitted from reactor. The rate constant of pig iron making per microwave power was $4 \times 10^{-3}\% \cdot s^{-1} \cdot kW^{-1}$.

The energy efficiency was 60% for heating resource s and the reduction of magnetite to wustite and 15% for the reduction of wustite to iron and molten pig iron. The concentrations of impurities of phosphorous and silicon in pig iron were much lower than those in pig iron of blast furnace because of vaporization during the reduction of iron ore under rapid heating and the low oxygen potential in existence with graphite powder. The sulfur content in pig iron was a little higher than blast furnace pig iron because of little slag.

KEY WORDS: pig iron making; magnetite; graphite; powder; microwave.

1. Introduction

Microwave is a coherent electromagnetic wave between 0.3 and 300 GHz and is absorbed by powdery material with electric polarization loss, magnetic loss and eddy current loss. Especially, microwave at 2.45 GHz is effectively absorbed by the mixed powder of iron oxide and carbon which generates heat themselves to produce molten pig iron.1) Because microwave locally generates heat inside of a material itself to make high temperature, the chemical reactions could proceed with much higher speed apparently at lower temperature than usual heating.2–4)

In the previous study by the present researchers,5) the continuous process of pig ironmaking was carried out using multi-mode microwave with 12.5 kW at 2.45 GHz and pig iron was successfully produced from the mixed powder of magnetite ore and coal, coke or graphite in a reaction chamber of MgO crucible. It was reported that the less microwave power relative to some mass of resources could only heat but not make reduction of iron ore by carbon.1,6) It has been realized that there could be a threshold value of power density of microwave to produce pig iron between 6.37 and 12.74 kW/m$^2$, as shown in Table 1. In lower power density than the threshold value, resources generated heat only to increase temperature, but in higher power density a reaction took place at about 1400°C.

Uniform electromagnetic field is produced from the multi-reflection of microwave on the wall surface of applicator that has the electromagnetic load. Thus, the applicator is constructed of steel or stainless steel to reflect microwave. However, the probability of absorption of microwave by resources is proportional to the volume ratio of resources to applicator. In order to make high density electromagnetic field, primary microwave beam should be radiated to resources. K. Ishizaki et al.7) found that the reduction of magnetite powder mixed with graphite powder proceeded more in the side of primary radiation of microwave than the opposite side.

In the present work, the furnace has been constructed to focus microwave beams into the center of applicator to make high density electromagnetic field and pig iron has been effectively produced.

2. Construction of Microwave Furnace

2.1. Applicator of Microwave

A coherent microwave of 2.45 GHz has the wavelength of 12 cm. An applicator with the integral size of wavelength forms steady state wave and the high and low density fields of microwave cyclically stand in the applicator. The steady state wave is impossible to heat resources uniformly. In order to avoid to make steady state wave, it is necessary that the shape of applicator is pentagon without parallel walls, the distance of parallel walls of applicator is out of the integral size of wavelength or the distance always changes by rotating fan.

During reflecting on the wall of applicator many times, a part of microwave backs to a microwave generator. The power of reverse microwave increases with increasing the
The smaller the size of applicator is, the higher the impedance increases. Thus, the applicable size of applicator is empirically realized to be at least more than five times of wavelength. In the case of microwave at 2.45 GHz, the size of applicator should be over 60 cm.

The applicator of stainless steel has sphere-like shape and is composed of a cylinder and two conic trapezoids with 1 m diameter and 1.2 m height, as shown in Fig. 1. 4 of 8 cylinders for antenna ports are installed on upper part of applicator and 4 lower part in direction to the center of applicator. The upper and lower antennas were dislocated by 45 degree each other in order to prevent microwave from interfering. There were 4 gates with 50 cm diameter in each of the top, bottom and both sides of applicator. The gate in each side had a safety switch to break electricity when the gate opens. The gate had a silica window with 10 cm diameter and copper mesh (25 mesh) inside in order to avoid microwave leakage. The gates in the top installed two water-cooled stainless pipes with the inside diameter of 2 cm for N₂ gas inlet and gas exhaust outlet, respectively. The edge of tubes was round with 1cm diameter in order to prevent from arcing. The applicator was evacuated by a vacuum pump and filled with N₂ gas from a gas inlet on wall.

2.2. System of Microwave Power Supply

The total of 20 kW microwaves were radiated into a furnace with circular polarized modes from eight helical antennas supplied by eight magnetrons oscillating at 2.450 ± 0.030 GHz with 2.5 kW each. The transmission lines consisted of magnetron-rectangular waveguide couplers (the cross-section of 55×109 mm), directional couplers, microwave vacuum windows and rectangular-coaxial waveguide mode converters. The water-cooled coaxial waveguides of copper with 28 mm diameter were terminated by helical antenna as shown in Fig. 2. The helical antenna is a stacked loop antennas that are axially aligned with small spacing and a few degrees of phase differences. Each loop antenna radiates waves to the axial direction. The radiations from loops interfere each other as a kind of phased array that forms a smaller radiation angles that is much better than a single loop or an open ended rectangular waveguide.

The power of forward microwave from each generator was controlled by on-off of pulse between zero to 2.5 kW and the percentage of microwave power to maximum was described by the parameter of generating rate (MWGR), \(\Theta_{MW}\);

\[
\Theta_{MW} = \frac{t_{on}}{10} \times 100 \% \quad \text{........................(1)}
\]

where \(t_{on}\) is the time during microwave irradiation in every 10 seconds.

2.3. Design of Antennas and Measurement of Radiation Angle of Microwave

The actual helical antenna was made of coiled stainless steel wire with 4 mm diameter. The diameter of loop was about 40 mm and 9 turns. The final shapes and dimensions of antenna were fixed experimentally to maximize the strength of forward microwave and minimize the radiation angles on the axis that was measured in the near fields. The vector network analyzer (VNA, Anritsu: MS2026A) feeds low power microwave to a the wave guide system (cold

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Power (kW)</th>
<th>Power density (kW/m³)</th>
<th>Max. temp. (°C)</th>
<th>Fe density in sample (g/cm³)</th>
<th>Time for max. temp. (s)</th>
<th>EMW (eV)</th>
<th>Note</th>
<th>Crucible</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.0</td>
<td>6.37</td>
<td>900</td>
<td>1.06</td>
<td>1800</td>
<td>0.34</td>
<td>Heating</td>
<td>Mullite</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>2.0</td>
<td>12.74</td>
<td>1370</td>
<td>0.94</td>
<td>900</td>
<td>0.76</td>
<td>Product</td>
<td>of pig</td>
<td>iron</td>
</tr>
<tr>
<td>3</td>
<td>3.0</td>
<td>19.11</td>
<td>1370</td>
<td>1.01</td>
<td>450</td>
<td>1.06</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>2.0</td>
<td>12.74</td>
<td>1370</td>
<td>1.06</td>
<td>1100</td>
<td>0.68</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>12.5</td>
<td>8.43</td>
<td>1400</td>
<td>1.10</td>
<td>2400</td>
<td>0.43</td>
<td>MgO</td>
<td></td>
<td>5</td>
</tr>
</tbody>
</table>
Radiated microwave was received by one turn loop antenna sweeping on a circle of 320 mm radius and measured by a spectrum analyzer (Agilent: E4407B).

For real high power operations, the radiation area of microwave in applicator was measured using a thermal paper set on a wood board painted with graphite powder in 5 mm thickness. A thermal paper of 50x600 mm was horizontally fixed in the center of applicator to the direction of the microwave generators of No. 7 and No. 5. Each generator radiated microwave during 3 seconds from helical antenna without load.

2.4. Tuning of Waveguide-coaxial Converter

Each waveguide-coaxial converter was tuned using VNA instead of microwave generator. VNA was connected to a waveguide-coaxial converter with an antenna through a rectangular waveguide. VNA radiated weak microwave between 2.4 and 2.5 GHz and the voltages of forward and reverse waves were measured.

The forward and reverse waves interfere each other to make a steady wave. Then, the ratio of the maximum amplitude of voltage, $|V_{\text{max}}|$, to a minimum one, $|V_{\text{min}}|$, so called the voltage standing wave ratio (VSWR), $\rho$, can be defined.

$$\rho = \frac{|V_{\text{max}}|}{|V_{\text{min}}|} = \frac{1 - |\Gamma|}{1 + |\Gamma|} \quad \text{(2)}$$

where $\Gamma$ is the ratio of voltage of reverse wave to that of forward one, so called “Reflection coefficient”. When VSWR is 1, there is no reflection of microwave. The maximum VSWR is practically 3 corresponding to 0.5 of the reflection coefficient. VSWR would be better to be less than 2. In order to minimize $\Gamma$ at 2.455 GHz, the length of back plate inserting depth, $b$, the inner conductor length, $l$, the location of plunger, $d$, and the gap between helical antenna and outer conductor, $h$, as shown in Fig. 2, were adjusted. Each waveguide-coaxial converter was installed on the applicator and $l$ was adjusted.

Each waveguide-coaxial converter with an helical antenna was installed on the applicator and connected to a microwave generator with 2.5 kW. Finally, its VSWR was measured with the load of water.

2.5. Pig Iron Making by Microwave Heating

2.5.1. Reactor

The reactor of pig iron making is shown in Fig. 3. The reactor was made of porous mullite bricks. The outside of reactor was in square with 23 cm side and the inside was in cylinder with 14 cm diameter and 6 cm depth. The inside wall and bottom of reactor were coated with MgO cement in 1 cm thickness. The lid was porous mullite board with 3 cm thickness and had 2 holes. The holes were $N_2$ gas inlet and exhaust gas outlet connected to water-cooled pipes, respectively. The reactor was dried in a microwave oven with 1 kW at 2.45 GHz for 75 min until no water was vaporized.

The temperature in the reactor was measured between 220°C and 1700°C using a mono-color pyrometer with the emissivity of 1.0 through the gas inlet tube.

The exhaust gas of $N_2$, CO and CO$_2$ was burnt in a burner. A part of gas was distributed to an oxygen sensor at 800°C to measure oxygen partial pressure in exhaust gas. The sensor was constructed with a 18 mol% CaO-stabilized ZrO$_2$ tube as solid electrolyte and air as reference electrode.

2.5.2. Procedure of Pig Iron Making

The reactor was set in the centre of applicator on the stand of porous mullite bricks. The water-cooled pipes were connected to the lid. The powders of iron ore, named “Romeral”, were dried in an electric oven at 150°C for one day and mechanically mixed with 18 mass% graphite in a ball mill for 6 hours. The ignition loss of graphite was 6.4%. 1 kg of the mixed powder was stamped in the reactor with several holes in order to release expanded gas during rapid heating.

After filling $N_2$ gas in the reactor, 50% (MWGR) of the microwave power was applied to start heating. During heating, MWGR was controlled to keep temperature less than 1500°C in order to prevent refractory from damaging. The aspects of reactor was monitored using a camera and recorded in a computer. After cooling the reactor, the weight loss of the reactor and resources by reaction was measured from the difference of weights before and after reaction. The state of residual reactant and product was visually observed. The plate, droplets and particles of pig iron were collected from the product in reactor after reaction. Dust was collected in...
the exhaust gas tube.

The chemical compositions of iron ore and graphite were analyzed using X-ray Fluorescence analyzer (XRF) and X-ray Difractometer (XRD), as shown in Table 2. The distributions of grain size before and after milling were measured using an optical microscope. Iron ore had 93.91 mass% of magnetite and graphite had 99.4 mass% of carbon. The chemical compositions of carbon and sulfur in pig iron were determined by means of the burning method of LECO (HF-400, S-444LS) and those of phosphorous and silicon in pig iron were measured using XRF.

3. Results

3.1. Shape and Radiation Angle of Helical Antenna and Parameters of Waveguide-coaxial Converter

The shape of helical antenna was determined as nine turns with the pitch distance of 8.3 mm and the diameter of 43.2 mm. The size of antenna was a little difference of ±2 mm each other. Table 3 shows the frequency, the strength of forward and reverse microwaves and VSWR of each generator.

Figure 4 shows the distributions of microwave strength as a function of angle from the direction of helical antenna with and without microwave absorber sheet, respectively. The absorber sheet makes the equivalent electromagnetic field to the free space. The measured radiation angles were ±37 degrees in the free space. On the other hand, the radiation angles were ±60 degrees from an open ended rectangular wave guide. The microwave power was 4–6 times higher on the axis than the rectangular open ended antenna.

The thermal papers heated by each microwave generator of No. 1 to 8 in the applicator without load were shown in Fig. 5. Most of black spots appeared within about 300 mm near the centre of applicator and some spots appeared at the edge of applicator because of no absorber of microwave. Therefore, microwave beams were focused into the area of about 300 mm diameter at the center of the applicator.

The parameters of waveguide-coaxial converter were determined as $b = 2.40$ mm, $d = 7.30$ mm, $h = 12.50$ mm and $l = 53.50$ mm (VSWR = 1.5).

3.2. Pig Ironmaking

By heating with the power of 17.5 kW during over 35 min, pig iron was successfully produced in 100% of the gain of iron from iron ore, as shown in Table 4. Figure 6 shows the changes of temperature in reactor, oxygen partial pressure in exhaust gas, forward and reverse microwave powers and MWGR.

The temperature rapidly rose above 850°C during first 4 min and after then gradually increased to 1 400°C with emitting bright and white light like ultraviolet rays. After 31 min, the temperature a little decreased. The oxygen partial pressure in exhaust gas, $pO_2$, drastically decreased to $1 \times 10^{-17}$ atm during first 4 min and was kept to be below $3 \times 10^{-15}$ atm. After 31 min, it increased to $5 \times 10^{-15}$ atm.

Table 2. Chemical compositions of iron ore and graphite and their distributions of grain size before and after milling.

<table>
<thead>
<tr>
<th>Composition/mass%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron ore</td>
</tr>
<tr>
<td>Fe</td>
</tr>
<tr>
<td>67.95</td>
</tr>
<tr>
<td>Graphite</td>
</tr>
<tr>
<td>Fixed C</td>
</tr>
<tr>
<td>93.05</td>
</tr>
</tbody>
</table>

Grain size/μm: >100 100–75 75–63 63–38 <38

- Before milling: Iron ore 6.4 16.4 52.0 25.0 0.2
- Graphite 43.4 14.6 5.7 17.6 18.7
- Milled mixture 3.0 41.8 29.7 19.2 6.3

The brand of iron ore is Romeral.

Table 3. Frequency and strength of forward and reverse microwaves and VSWR of each generator.

<table>
<thead>
<tr>
<th>Generator No.</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Frequency/GHz</td>
<td>2.456</td>
<td>2.454</td>
<td>2.453</td>
<td>2.455</td>
<td>2.455</td>
<td>2.455</td>
<td>2.455</td>
<td>2.454</td>
</tr>
<tr>
<td>Forward power/kW</td>
<td>2.64</td>
<td>2.81</td>
<td>2.98</td>
<td>2.72</td>
<td>2.55</td>
<td>2.79</td>
<td>2.63</td>
<td>2.64</td>
</tr>
<tr>
<td>Reverse power/kW</td>
<td>0.21</td>
<td>0.17</td>
<td>0.35</td>
<td>0.22</td>
<td>0.18</td>
<td>0.04</td>
<td>0.19</td>
<td>0.33</td>
</tr>
<tr>
<td>VSWR</td>
<td>1.79</td>
<td>1.65</td>
<td>2.04</td>
<td>1.79</td>
<td>1.72</td>
<td>1.27</td>
<td>1.74</td>
<td>2.09</td>
</tr>
</tbody>
</table>

VSWR is voltage standing wave ratio that means the ratio of the maximum amplitude of microwave voltage to the minimum one.
While the power of forward microwave was stable to be 2.5 kW, the power of reverse one increased to 1 kW at first time, gradually decreased during 4 min and kept at about 0.5 kW. Pig irons were produced in the bottom of reactor, as shown in Fig. 7. During 14 min of heating time, a little pig iron particles were produced. After 30 to 35 min, the gain of pig iron was almost 80% but sintered product was remained in the center of bottom. After 46 min, resources completely reacted to produce pig iron with the gain of 100%.

The concentrations of carbon, sulfur, silicon and phosphorous in pig iron are listed on Table 5. The carbon content was 2.56 to 2.82 mass% in the hypo-eutectic region of iron-carbon alloy, because the droplets of molten pig iron rapidly flowed down to the bottom of reactor to separate from graphite powder.

A little slag of 2.31 g to 4.23 g was adhered on the surface of pig iron in spots. Residual graphite powder were found in dust and stuck on the wall of reactor. Dust was 0.8 g to 6.4 g in weight and had carbon. Most of all residual carbon according to a little temperature decrease. While the power of forward microwave was stable to be 2.5 kW, the power of reverse one increased to 1 kW at first time, gradually decreased during 4 min and kept at about 0.5 kW. Pig irons were produced in the bottom of reactor, as shown in Fig. 7. During 14 min of heating time, a little pig iron particles were produced. After 30 to 35 min, the gain of pig iron was almost 80% but sintered product was remained in the center of bottom. After 46 min, resources completely reacted to produce pig iron with the gain of 100%.

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<table>
<thead>
<tr>
<th>Products</th>
<th>Run No.</th>
<th>Chemical compositions/mass%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>C</td>
</tr>
<tr>
<td>Pig iron</td>
<td>D-2</td>
<td>2.56</td>
</tr>
<tr>
<td></td>
<td>D-3</td>
<td>2.48</td>
</tr>
<tr>
<td></td>
<td>D-4</td>
<td>2.76</td>
</tr>
<tr>
<td></td>
<td>D-5</td>
<td>2.22</td>
</tr>
<tr>
<td></td>
<td>D-6</td>
<td>2.82</td>
</tr>
<tr>
<td>Dust</td>
<td>D-2</td>
<td>49.08</td>
</tr>
<tr>
<td></td>
<td>D-3</td>
<td>33.5</td>
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<tr>
<td></td>
<td>D-4</td>
<td>36.84</td>
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<tr>
<td></td>
<td>D-5</td>
<td>30.66</td>
</tr>
<tr>
<td></td>
<td>D-6</td>
<td>23.59</td>
</tr>
<tr>
<td>Residual</td>
<td>D-4</td>
<td>32.56</td>
</tr>
<tr>
<td></td>
<td>D-5</td>
<td>35.25</td>
</tr>
<tr>
<td></td>
<td>D-6</td>
<td>49.00</td>
</tr>
</tbody>
</table>

Composition of Slag for No. 6/mass%:

<table>
<thead>
<tr>
<th></th>
<th>SiO₂</th>
<th>MgO</th>
<th>Al₂O₃</th>
<th>CaO</th>
<th>FeO</th>
<th>MnO</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>49.7</td>
<td>20.8</td>
<td>13.9</td>
<td>10.7</td>
<td>1.3</td>
<td>0.69</td>
</tr>
</tbody>
</table>
powder was scraped out of cement on the surface wall of reactor after reaction. The chemical compositions of dust and residual in reactor are shown in Table 5.

4. Discussions
4.1. Distribution of Microwave Power Density in Reactor
Primary radiation of microwave from 8 helical antennas was concentrated into the area of about 300 mm diameter at the center of applicator. As the maximum power was 20 kW, the maximum density of power was about 1 400 kW/m³. This high power density was enough to proceed the production of pig iron from the mixture of magnetite and graphite powders. However, the microwave radiation was not uniform. In case of the microwave power of 17.5 kW, No. 3 microwave generator was turned off. Pig iron was less produced in the side of No. 3 microwave generator than the other side, as shown in the samples No. D-2 and D-3 of Fig. 7. This indicates that the primary radiation is efficiently absorbed into resources. Thus, in order to obtain the uniform distribution of microwave field in reactor, MWGR should be controlled using 8 generators.

The lower side of product plates of D-2 and D-3 had the layer of sintered powder in the direction of No. 6 and No. 8 generators. This indicated that microwave field was weakened near the layer. Because there was the frequency difference of 1 MHz between No. 6 generator with 2.455 GHz and No. 8 with 2.454 GHz and no difference between other two generators with 2.455 GHz, the interference of microwave probably took place to strengthen or weaken the field near the bottom of reactor.

4.2. Mass Balance of Iron and Carbon
The amount of pig iron including carbon produced from 1 kg of resources was calculated to be 572.6 g for D-4 and 570.0 g for D-5. Comparing the measured weights of pig iron in Table 4, 100% of iron in resources was obtained as pig iron. Dust was composed of graphite powder. In the case of D-6, 45.2 g of magnetite ore was dispersed.

The apparent reaction can be expressed as the following equation;

\[
\text{Fe}_3\text{O}_4 + (x+y)\text{C} \rightarrow 3\text{Fe} + x\text{CO} + y\text{CO}_2
\]

where

\[
x + 2y = 4
\]

from the mass balance of oxygen and the restrictions of \(x\) and \(y\) are \(4 \geq x \geq 0\) and \(2 \geq y \geq 0\), respectively.

As the percentage of magnetite in ore is calculated to be 94.1 mass% from the percentage of total Fe, the amount of magnetite in resources is 3.352 mol. The weight of graphite powder was 180 g including the ignition loss, \(I\), and carbon in dust and residue of reactor, \(z\). The mole ratio of carbon to magnetite is expressed as

\[
\frac{180 \times (1-I) \times 0.9941 - z}{12} : 3.352 = (x + y) : 1
\]

From the Eqs. (4) and (5), using \(I = 0.064\) and \(z = 10.98\) g, one obtains \(y = 0.1698\) and \(x = 3.660\) for D-4 and \(y = 0.1398\) and \(x = 3.720\) using \(z = 8.573\) g for D-5. From these values of \(y\), the mean partial pressure ratios of CO gas to CO and CO₂ gases during reaction are obtained to be 0.956 for D-4 and 0.964 for D-5, respectively.

The weight loss of resources except dust was caused from the evaporation of CO and CO₂ gases according to the Eq. (3). The following mass balance is obtained using the measured weight loss, \(\Delta W\), including water of crystallization in cement, \(W_{\text{H}_2\text{O}}\),

\[
\Delta W - W_{\text{H}_2\text{O}} - Z = 3.352 \times (28x + 44y) \quad \quad (6)
\]

where \(Z\) is the weight of dust. One obtains \(W_{\text{H}_2\text{O}} = 37.8\) g for D-4 and 37.4 g for D-5.

4.3. Mass Balance of Impurities
The amount of phosphorus in magnetite ore of 820 g was 0.107 g. Total amount of phosphorus in pig iron and dust was 0.0412 g and 0.0305 g for D-4 and D-5, respectively. Phosphorus in dust was 0.0006 g for D-4 and 0.0015 g for D-5 and that in slag was negligible small. Because of low oxygen partial pressure under the existence of graphite and no usage of lime to make little slag, phosphorus in magnetite ore could be taken out in exhaust gas during heating before producing pig iron. The percentage of phosphorous of 0.0071 and 0.0051 mass% in pig iron was much lower than 0.1 mass% in pig iron of blast furnace.

The amount of sulfur in 820 g of magnetite ore was 1.22 g. Total amount of sulfur in pig iron and dust was 0.79 g for D-4 and 0.55 g for D-5, respectively. Most of sulfur dissolved into pig iron. Some part of sulfur was vaporized and absorbed in dust. The sulfur content of about 0.15 mass% in pig iron were higher than 0.04 mass% in pig iron of blast furnace because of the lack of lime and slag.

The amount of silicon in ore was 10.62 g. For D-6, the amounts of silicon in pig iron, slag, dust were 0.352 g, 0.983 g and 0.054 g, respectively. The total amount of silicon in products was 1.389 g and was much lower than that in ore. It was possible that silica in ore could be vaporized as SiO gas, because of the existence of graphite and the lack of lime.

4.4. Reaction Process of Pig Iron Making
Figure 8 shows the phase diagram of Fe–C–O system with the Boudouard reaction of CO₂+C→2CO as the relation

Fig. 8. Reduction process of magnetite ore with graphite on the phase diagram of Fe–O–C system.
of temperature to the partial pressure ratio of CO gas to the sum of CO and CO$_2$ gases. The partial pressure ratio of CO$_2$ to CO is thermodynamically calculated from the partial pressure of oxygen measured by oxygen sensor in Fig. 6 according to the reaction of $2\text{CO} + \text{O}_2 \rightarrow 2\text{CO}_2$. The reaction process of the present work is shown in Fig. 8.

During first 4 min, magnetite was stable from room temperature to 850°C and magnetite and graphite powders generated heat to increase temperature. After 4 min until 6 min, magnetite was rapidly reduced to wustite with increasing temperature from 850°C to 950°C. When temperature increased from 950°C to 1400°C, wustite was endothermically reduced to iron. Over 1200°C, reduced iron directly absorbed carbon from graphite to produce pig iron particles. After 30 min, pig iron particles gathered themselves to make droplets of pig iron and flowed down into the bottom of reactor. Because pig iron droplets reflected microwave, temperature decreased a little.

4.5 Efficiency of Energy Usage

During first 4 min, there was no reaction but temperature of resources increased from room temperature to 850°C. The heat absorbed by 1 kg of the mixed powder of magnetite and 18 mass% graphite is calculated from their heat capacities$^8$ to be 872 kJ. The reverse power of microwave was about 0.8 kW for a generator, while the forward power was 2.5 kW. Then, the net power of microwave was about 0.5 kW and the forward power was 2.5 kW. Then, the required heat of reduction and carburization can be calculated according to the following equation;

$$\Delta H^0_1 = \Delta H^0_{1,298} - \int_{298}^{1023} (3C_{\text{Pr},i} + 2C_{\text{Pr}})dT$$

$$+ \int_{298}^{1123} (9C_{\text{Pr},i} + C_{\text{Pr}} + C_{\text{Pr}})dT$$

where $\Delta H^0_{1,298}$ is the standard enthalpy of reaction (7) at 298 K, $C_{\text{Pr}}$ is the heat capacity of i element and T is the absolute temperature. $\Delta H^0_1$ is calculated to be 424.6 kJ. As 820 g of magnetite in resources is 3.562 mol, the required heat is 503.9 kJ. During 2 min, the reverse power of microwave was about 0.5 kW and the forward power was 2.5 kW. Then, the net power of microwave was 7.00 kW corresponding to 13440 kJ. Thus, 15.6% of net microwave energy was used for the reduction. This result is caused from slower Boudouard reaction than the reduction of wustite to iron, because the process proceeded in higher temperature side than the Boudouard reaction, as shown in Fig. 8.

Over 1200°C, reduced iron was actually carburized to make pig iron. However, as shown in Fig. 8, the gas ratio CO/(CO+CO$_2$) in gas phase against temperature proceeded on the carbon activity of 0.05 and crossed the liquidus line of pig iron at about 1500°C. This means that reduced iron absorbs carbon to make molten pig iron from solid carbon at a point of contact with iron instead of gas phase, as realized by T. Murakami et al.$^{10}$

4.6 Reaction Kinetics

Figure 9 shows the yield of iron produced from magnetite ore and the weight loss of resources as a function of time. For D-1, 57.6 g of pig iron was obtained after 14 min. In this stage, temperature attained at 1200°C and apparently magnetite was reduced to wustite and partially to iron by carbon.

Fe$_3$O$_4$+C→3FeO+CO ....................... (13)

Fe$_2$O$_4$+4C→3Fe+4CO ....................... (14)

FeO+CO→Fe(liquid)+CO$_2$ .................... (9)

and the Boudouard reaction

CO$_2$+C→2CO .......................... (10)

Then, the apparent reaction is expressed as

FeO+C→Fe(liquid)+CO ...................... (11)

$$\Delta H^0_1 = \int_{298}^{1023} (3C_{\text{Pr},i} + 2C_{\text{Pr}})dT$$

$$+ \int_{298}^{1123} (9C_{\text{Pr},i} + C_{\text{Pr}} + C_{\text{Pr}})dT$$

$\Delta H^0_1$ is calculated to be 195.8 kJ. As FeO is 10.686 mole, the required heat is 2092.3 kJ. From 6 min to 38 min, the reverse power of microwave was about 0.5 kW, while the forward power was 2.5 kW. Then, the net power of microwave was 7.00 kW corresponding to 13440 kJ. Thus, 15.6% of net microwave energy was used for the reduction. This result is caused from slower Boudouard reaction than the reduction of wustite to iron, because the process proceeded in higher temperature side than the Boudouard reaction, as shown in Fig. 8.

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Fig. 9. Yield of iron produced from magnetite ore by microwave radiation with 17.5 kW and 20 kW, respectively, and the weight loss of resources as a function of time.
Assuming the carbon content of 2.5 mass% in pig iron, FeO of 76.57 g is consumed. According to the Eq. (14), the weight loss by CO gas is 37.25 g. As the weight of net magnetite in ore is 771.62 g, 695.05 g of Fe₃O₄ is consumed and the weight loss according to the Eq. (13) is 84.54 g. Total weight loss is 121.8 g and in good agreement with the measured value of 120.2 g including 0.8 g of dust. In this early stage, water of crystallization in cement had not yet been decomposed.

The weight loss and the gain of iron linearly increased with time according to increasing until near 1400°C. The apparent reaction rate is 0.0667%·s⁻¹ under the microwave power of 17.5 kW and 0.0833%·s⁻¹ under 20 kW. The apparent reaction rate increased with increasing the microwave power. This indicates that the reaction rate could be controlled by energy supply. Assuming that the microwave power decreases exponentially from the surface of resources because the energy is absorbed into the resources, the reaction rate can be expressed as the following equation;

\[
dw_{\text{Fe}} = k' I_0 \quad \text{(15)}
\]

where \(w_{\text{Fe}}\) is the amount of produced iron in unit volume at the distance of \(x\) from the surface of resources. \(k'\) is the reaction rate constant. \(I_0\) is the microwave power and expressed as \(I_0 = 1_0 e^{-\alpha x}\). \(\alpha\) is the microwave power at the surface of resources, \(\alpha\) is the absorption coefficient. The rate of the total amount of reduced iron can be obtained by integrating the Eq. (15) over the volume of resources. Dividing by the amount of total iron in resources, \(W_0\), and expressing in%, one obtains

\[
\frac{d(\%)}{dt} = \frac{S}{100W_0} \int_0^1 dw_{\text{Fe}} dx = \frac{S}{100W_0} k_0 I_0 \int_0^1 e^{-\alpha x} dx = k I_0 \quad \text{(16)}
\]

assuming that \(I_0\) is larger than the penetrating depth of microwave. \(S\) is the surface area of resources.

Therefore, the reduction rate of iron ore is proportional to the microwave power at the surface of resources. From the present data, \(k = 4 \times 10^{-9} \text{B}^2 \text{s}^{-1} \text{KW}^{-1}\).

### 4.7. Effect of Microwave on Reaction

During the reduction of wustite to iron, bright and white light like luminescence was emitted from reactor. A. Matsubara et al. measured the spectrum of the light emitted from the reduction of magnetite powder with graphite powder heated over 1260°C by microwave with 2.5 kW at 2.455 ± 0.030 GHz. They found that almost of the peaks between 248 nm and 302 nm were assigned to the spectra of electronic de-excitation of iron atom observed in arc and spark discharges, as listed in Table 6. The excited iron atoms were in the upper levels of 4.2 to 5.0 eV. When electron shifted to the base level of iron from the upper level, light with the specific wave length was emitted. The first and second ionization energies of iron are 7.87 eV and 16.18 eV, respectively. Therefore, Fe²⁺ ion discharged to be the excited iron atoms, Fe⁺, through the state of Fe²⁺ and then de-excited to be the ground state of Fe⁰ with emitting light.

| Table 6. Spectra data between 248 to 302 nm and transition levels of Fe produced from magnetite ore by microwave heating (After A. Matsubara). |
| ---------------------------------- | -------- | -------------- | --------- | --------- |
| Atom | Wave length (nm) | Level energy (eV) | Distribution of electron |
| Fe I | 248.28 | 248.3 | 0.000000 | 4.0912705 3d6.4s2 3d6.5D.4s.4p(1P⁰) |
| Fe I | 252.27 | 252.3 | 0.000000 | 4.9129732 3d6.4s2 3d6.5D.4s.4p(1P⁰) |
| Fe I | 271.89 | 271.9 | 0.000000 | 4.5585225 3d6.4s2 3d6.5D.4s.4p(1P⁰) |
| Fe I | 274.3 | 274.2 | 0.0872857 | 4.6069507 3d6.4s2 3d6.5D.4s.4p(1P⁰) |
| Mn I | 279.53 | 279.5 | 0.000000 | 4.434911 3d5.4s2 3d5.6S.4s.4p(1P⁰) |
| Na I | 285.18 | 285.3 | 0.000000 | 4.344759 2p6.3S 2p6.5P |
| Fe I | 296.72 | 296.8 | 0.110114 | 4.2843477 3d6.4s2 3d5.4F.4p(1P⁰) |
| Fe I | 302.05 | 302.1 | 0.110114 | 4.2088830 3d6.4s2 3d5.4S.4p(1P⁰) |

Note: The ground state of iron is 3d6.4s2.

\[\text{Fe}^{2+} + 2e^- \rightarrow \text{Fe}^*(\text{excited}) \quad \text{(17)}\]

\[\text{Fe}^*(\text{excited}) \rightarrow \text{Fe}^0(\text{ground state}) + h\nu \quad \text{(18)}\]

where \(h\) is the Planck’s constant and \(\nu\) is the number of wave. Therefore, these spectra are the signal of iron production at high temperature under microwave radiation, while such spectra were not observed in blast furnace.

The activation energy of reduction of FeO with CO gas is about 81 kJ·mol⁻¹, corresponding to about 0.42 eV, and the frequency factor, \(\omega_0\), is \(1 \times 10^{11} \text{s}^{-1}\).

\[\text{FeO} + \text{CO} \rightarrow \text{Fe} + \text{CO}_2 \quad \text{(19)}\]

When 2 electrons activated by microwave and heat get the energy over the activation energy, the reaction proceeds. The thermal energy of electron, \(k_B T\), is the order of 0.1 eV at 1400 K, where \(k_B\) is the Boltzman constant. Assuming that the microwave energy absorbed into sample is proportional to the volume ratio of sample to applicator, the activated energy of electron by microwave, \(E_{\text{MW}}\), can be calculated and are listed in Table 1.

\[E_{\text{MW}} = \frac{\alpha (\text{Power density}) M_{\text{Fe}}}{2(\text{Fe density in sample}) \omega} \quad \text{(20)}\]

where \(\alpha\) is the efficiency of microwave absorption into sample and 15.6%. \(M_{\text{Fe}}\) is the atomic weight of iron. \(\omega\) is the frequency factor of reaction under microwave irradiation and can be expressed as

\[\omega = \omega_0 \exp \left( \frac{E_{\text{MW}}}{h\nu} \right) \quad \text{(21)}\]

where \(\nu\) is the specific number of wave and \(5 \times 10^{13} \text{s}^{-1}\). The physical meaning of the specific number of wave is not clear but seems to be the number of acoustic wave in crystal generated from spin resonance by microwave.

The threshold energy to proceed reaction by microwave seems to be 0.42 eV of the activation energy.

### 5. Conclusion

Radiating primary microwave with total 20 kW from 8 microwave generators at 2.455 GHz into the center of furnace, 1 kg of mixed powder of magnetite and 18 mass% graphite rapidly produced molten pig iron with 100% of the
gain of iron at about 1400°C during 30 min. Temperature drastically increased to 950°C during 6 min and magnetite was reduced to wustite. After then wustite was gradually reduced to iron with emitting of luminescence. The reduction rate was proportional to microwave power and the rate constant per kW was $4 \times 10^{-3} \text{s}^{-1} \text{kW}^{-1}$. The concentrations of impurities such as phosphorous and silicon in pig iron were much lower than those in pig iron of blast furnace because of vaporization during the reduction of iron ore under rapid heating and less slag.

REFERENCES

12) A. Matsubara: Private communication, June 16, 2012.