Mechanism of Carbothermic Reduction of Fe$_3$O$_4$ Irradiated by Microwave with 2.45 GHz

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The reaction mechanism of the carbothermic reduction of Fe$_3$O$_4$ powder heated by radiating multi-mode microwave with 2.45 GHz and 2.8 kW was clarified by means of gas analysis and changing the contact state of mixed powder. The reaction process was classified in three stages. In the stage I, the powder was heated by the magnetic loss of Fe$_3$O$_4$ and the induction current loss of graphite (Gr) and reached peak temperature of 1000$^\circ$C to 1200$^\circ$C in 30 s to 40 s after irradiation, and then dropped rapidly at 600$^\circ$C to 700$^\circ$C. Fe$_3$O$_4$ was reduced to FeO. In the stage II, the powder was heated by the induction current loss of FeO and Gr, and the entropy production was maximum after about 100 s. In the stage III, molten pig iron was produced with light emission. The reaction rate was always larger for the Boudouard reaction than the reduction of Fe$_3$O$_4$ or FeO. This indicates that the Boudouard reaction is preferentially promoted by microwave near the contact points between Gr particles. The dominant reactions were determined to be Fe$_3$O$_4$+CO→3FeO+CO$_2$, FeO+CO→Fe+$\Delta$CO$_2$ and the Boudouard reaction from the smaller negative value of the Gibbs energy change of reactions. In the stage I and III, the pre-exponential factor of reaction rate increased with time. In the stage II, the apparent activation energy of reduction rate of iron oxide heated by microwave was lower than conventional heating.

KEY WORDS: magnetite; carbothermic reduction; microwave; reaction mechanism; pig iron.

1. Introduction

When producing 1 ton of pig iron in a Japanese blast furnace, about 2.2 tons of CO$_2$ caused by fossil fuels are emitted. In blast furnace, the heat of combustion of coke is used to heat raw materials and supplied to promote the endothermic reduction of iron ore. K. Nagata et al.$^{1–4}$ proposed a method to utilize the energy generated by microwave irradiation in spite of the combustion heat. As a result, the amount of carbon consumption decreased by mass balance required for the reduction of iron ore, and the amount of CO$_2$ gas generated became half. By this method, a continuous pig-ironmaking system producing 240 kg of pig iron per day$^5$ and a rotary furnace for pig-ironmaking$^4$ were developed. The utilization efficiency of microwave power of 40% was obtained.$^5$

For blast furnace it is necessary to use special high-strength lumpy raw materials to maintain the permeability of hot gas. For pig-ironmaking by microwave irradiation, there is no such restriction of materials because powder can be used. Moreover, since the specific surface area of powder is about 200 times larger than lumpy materials, the reaction rate of powdery iron ore becomes much faster than lumpy materials. In a modern blast furnace, it takes 6 to 8 hours from loading raw materials to tapping of pig iron, but in pig-ironmaking by microwave irradiation, it takes about 15 minutes. Therefore, the furnace could be compact.

Since phosphorus evaporates in the process of rapidly heating raw materials by microwave, it is not necessary to add limestone to them. Therefore, almost no slag is produced, and no heat is necessary to heat slag.

The raw materials absorb microwave rapidly to generate heat themselves, while in blast furnace with heating materials by high-temperature gas, heat slowly conducts from the surface of materials to the inside. As in blast furnace, work of chemical reaction is extracted from heat obtained by burning coke, the conversion efficiency of work from heat is constrained less than almost 40% due to the Carnot’s law. On the other hand, by microwave irradiation, energy generates as work in materials and can be converted to heat and work of chemical reaction. Therefore, the conversion of work to work theoretically can be 100% due to the Joule’s law.

Such a faster reaction rate by microwave irradiation than the conventional heating is called “Microwave effect”, but its mechanism has not been clarified.
The study by N. Standish et al. first showed that the carbothermic reduction of iron oxide by microwave irradiation is faster than that of conventional heating by external heat. K. Ishizaki et al. heated carbon-composite pellets (20 mm in diameter, about 8 g per one pellet) in N₂ gas by multi-mode microwave with 2.45 GHz. At 3 kW, temperature of a pellet increased by 2.7°C/s and reached about 1350°C in 500 s, and molten pig iron was produced. When microwave intensity was gradually increased to heat pellets relatively slow, Fe₂O₃ was reduced to FeO at 800°C to 1000°C, FeO was reduced to Fe at 1000°C to 1250°C and molten pig iron was produced. It was also shown that the higher the rate of temperature rose, the lower the concentration of impurities such as phosphorus and sulfur in pig iron and the higher the concentration of carbon became.

About 6 g of mixed powder of Fe₂O₃ with about 1 μm diameter and carbon black with 22 μm diameter was irradiated by multi-mode microwave with 2.8 kW and 2.45 GHz. The reaction process was divided into three stages. In the first 40 seconds, Fe₂O₃ particles generated heat and temperature rose to about 800°C. Carbon black generated heat in all processes. Temperature was maintained for the next about 50 s. After then temperature rose and molten pig iron was produced in about 300 s. Fe₂O₃ was reduced to FeO at 400°C, and FeO was reduced to Fe at 800°C. In the first stage, CO₂ gas generated more than CO gas, and it was indicated a solid-solid reaction of Fe₂O₃ and carbon black to produce FeO and CO₂ gas. The rate of mass reduction of resources in the first stage was faster than that of FeO to Fe in the second and third stages at high temperature. The reduction reaction occurred from the surface of pellet to the inside, and the carbon concentration in iron locally varied from 0 to 2 mass%. This was caused by local absorption and attenuation of microwave.

N. Sabelström et al. heated a carbon-composite pellet by irradiating single-mode microwave with 2.45 GHz and measured the individual temperature of each component from its thermal expansion of lattice spacing. In the first stage, microwave in magnetic field was absorbed by Fe₂O₃ and temperature became about 100°C higher than the average temperature measured on the surface of sample. In the next stage, it became lower than the average temperature during the reduction to FeO in both magnetic and electric fields. After then the temperature of FeO exceeds the average temperature at about 1000°C in magnetic field. Carbon absorbed microwave in both magnetic and electric fields to generate heat, and the temperature of carbon gradually rose over the average temperature.

M. Hayashi et al. showed that the higher the bulk density of the mixed powder was, the lower the steady-state temperature was. M. Hotta et al. measured the complex magnetic permeability and complex permittivity of carbonaceous materials and iron oxide powder depending on temperature and frequency. Permeability decreased with increasing frequency and decreased sharply at the Curie temperature of 585°C. The frequency dependence of the permittivity was small, but its imaginary part increased sharply at the Curie temperature. These values increased when the bulk density increased. This indicates that when the bulk density of the raw material increases, microwave is absorbed near the surface and the penetration depth becomes shallower.

A. Matsubara et al. detected the excitation spectrum of CN gas in the first stage of heating and further detected the excitation spectrum of iron in the third stage by multi-mode microwave irradiation. It is possible that CN gas contributes for the solid-solid reaction between Fe₂O₃ and carbonaceous material in the early stage of microwave irradiation.

K. Hara et al. showed that there was a threshold value of power density of microwave to produce pig iron between 6.37 and 12.74 kW/m³ and the activation energy of reduction from FeO to Fe was 0.42 eV (40.5 kJ/mol).

K. Nagata et al. showed that the carbothermic reduction of Fe₂O₃ by microwave irradiation also proceeded. Since α-Fe₂O₃ is paramagnetic, it hardly generates heat even when irradiated by microwave at room temperature. But, when it was heated to 400°C, heat started to generate due to induced current in magnetic field, and temperature rose rapidly.

As mentioned above, by microwave irradiation, the carbothermic reduction of Fe₂O₃ and Fe₂O₃ is much faster than conventional heating and molten pig iron is produced. One of the reasons for these phenomena could be that as materials absorb microwave to generate energy themselves, the contact state between solid materials has influence on the rate of temperature rise and the reaction rate.

2. Experiments
2.1. Microwave Heating Furnace

The microwave furnace (Kyoei Electric Kilns, MS-1) is shown in Fig. 1. It had two microwave generators with 600 W magnetron device and added two generators (P. S. Engineering, PSMM-2K0401) with 800 W magnetron device (Panasonic, 2M244-M1). The experiment was conducted with 2.8 kW. The applicator was formed pentagonal, and multi-mode microwave was used.

The reaction tube of recrystallized quartz was installed horizontally. For sampling produced gas rapidly, a silica tube spacer was inserted in the inlet side of reaction tube to reduce the volume of the reaction tube and the tube was narrow in the outlet side, as shown in Fig. 2. The volume from reaction site to gas sampling position was 34.746 ml, and the arrival time of reaction gas was corrected by the flow rate of total gas.

An Al₂O₃ crucible including 3 mass% SiO₂ with 24 mm
height, 15 mm outer diameter and 10 mm inner diameter was used for reaction. The crucible was set in a refractory block (Isolite Ind., LBK-3000) for keeping heat. The composition of isolite is shown in Table 1. It was confirmed that the silica tube, crucible and block did not absorb microwave to generate heat under the experimental conditions. The isolite brick was used keeping heat in reaction crucible.

2.2. Samples

Table 1 shows the composition of magnetite and graphite (Gr) analyzed by a fluorescent X-ray (XRF). Two types of magnetite, (a) and (b) (Soegawa Rikagaku, purity 99% and High Purity Chemical Laboratory, purity 99.9%, respectively) were used. The particle sizes of (a) and (b) were 1 μm and 180 μm or less, respectively. The average particle size of Gr (Kishida Chemical, purity 99%) was 75 μm.

Table 2 shows the mixing ratio of magnetite and Gr. In Series A, the mixing ratio was changed, and magnetite (a) was used. A-1 had the molar mixing ratio of 1: 5, and A-2 to A-4 had the ratio in the cases that the generated gas was all CO, CO and CO2 in equimolar and all CO2, respectively, and adding 3 mass%C in pig iron.

In Series B, the diameter of magnetite powder was changed. The mixing ratio in Series B and Series C was same as that of A-2. For B-1, magnetite (a) with a particle size of 1 μm and 180 μm or less, respectively. The average particle size of Gr (Kishida Chemical, purity 99%) was 75 μm. B-1 and C-1 are the same sample. Mean particle size of graphite is 75 μm. B-1 and C-1 are the same sample.

In Series C, the mixture of magnetite (a) and Gr was milled. The milling time for C-1 to C-3 was 0 min, 60 min, and 180 min, respectively. B-1 and C-1 were the same experiment.

The powder of magnetite and Gr was mixed in a mortar of stainless steel. For C-2 and C-3 it was further milled in a vibrating ball mill. In milling, 9 g of powder was put in an alumina container having recrystallized alumina balls with 5.3 mm diameter by 50 volume%. The container was constructed with two recrystallized alumina crucibles bonded with an adhesive.

2.3. Experimental Method

3 g of mixed powder was set in a crucible with a little vibration, and several vent holes were made for freeing from gas expansion. The height of mixed powder was about 20 mm. The relative bulk density was about 40%. The crucible was placed in a reaction tube. After evacuating the inside of tube twice with a vacuum pump, N2 gas (purity more than 99.9995%) was filled. During the experiment, N2 gas was flowed at the flow rate of 100 ml/min. The microwave power was increased to 2.8 kW during 25 s after the start of microwave irradiation.

Gas sampling was performed every 10 s during first 3 min, every 15 s from 3 min to 4 min, every 30 s thereafter and even after stopping microwave irradiation. Gas of about 2.0 ml was sampled in about 2 s from the sampling point shown in Fig. 1 using a micro-syringe (Ito Seisakusho, Microsyringe MS-GAN250).

All exhaust gas during the experiment was collected by two sampling bags (AS ONE, Tedlar bag with one mouth cock, capacity of 3 l) shown in Fig. 1, and the volume and the composition of gas were measured.

A gas chromatograph (Shimadzu, GC-8APT; CG) was used for gas analysis using Ar gas as carrier gas. The CG data was output to PC using a chromatographic pack (Shimadzu, C-R8A). The data was recorded on a PC and a data logger.

It took about 20 min to analyze one syringe. About 30 gas

![Fig. 2. Schematic illustration of reaction chamber. (Online version in color.)](image)
samples were collected in one experiment and it took about 10 hr to complete all the analysis. The tip of the needle of syringe was sealed with silicone rubber until it was analyzed by CG, but it was not perfect, and air entered a little. Therefore, the amount of air mixed in was calculated from the concentration of O₂ in sampling gas, and the concentration of N₂ gas was corrected. The corrected gas composition is (CO%) + (CO₂%) + (N₂%) = 100. The composition of air was analyzed to be 20.64% O₂ and 79.36% N₂.

The weight loss of sample was determined from the weight of the crucible with sample before and after reaction. The concentration of carbon and sulfur in pig iron was measured with a carbon-sulfur simultaneous analyzer (Leco, HF-400, CS-44LS).

Temperature at the center of the sample surface in a range of about 6 mm diameter was measured with an optical thermometer (Japan Sensor, FTK9-P300R-50L21) from the top of the furnace through a hole in brick, as shown in Fig. 1. The thermometer was able to measure over 220.6°C.

3. Results

Temperature and the concentration of CO and CO₂ in exhaust gas for Series A, Series B and Series C are shown in Figs. 3 to 5, respectively. From these results, the reaction stages can be classified into three.

In the stage I, heat was generated by the magnetic loss of microwave due to Fe₃O₄, and temperature rose rapidly. Temperature reached maximum at 1000°C to 1200°C after 30 s to 40 s from starting microwave irradiation, and after then it dropped rapidly at 600°C to 700°C in 40 s to 50 s. The concentration of CO₂ gas increased more than that of CO gas during temperature rise and reached maximum and then gradually decreased. In this stage, Fe₃O₄ was reduced to FeO.

In the stage II, heat was generated by induced current in FeO and Gr, and the concentration of CO gas increased continuously and reached maximum in about 100 s.

In the stage III, temperature gradually rose or stagnated and reached at 1200°C to 1500°C. In the early stage, molten pig iron was produced with light emission, The concentrations of CO gas and CO₂ gas decreased and became to almost zero after about 300 s. Temperature of B-2 was unstable because a part of Gr powder adhered to the inner wall of the quartz tube, making accurate temperature measurement impossible.

Table 3 shows the amount of mass loss of the samples due to reaction, the total amount of exhaust gas, and the concentration of gas components. The total mass of CO gas and CO₂ gas in exhaust gas agreed with the mass loss of the sample within 99% to 113%.

Figure 6 shows the results of XRD analysis of mixed materials for B-1 on the way of temperature rise. The sample weight was 3.0 g. XRD spectrum (a) in the figure is at the maximum temperature of 900°C in the stage I, (b) is at the temperature dropped rapidly to 650°C in the end of the stage I, and (c) is at 1100°C on the way of temperature rise with the rate of 8°C/s in the beginning of the stage III after 83 s.

Fe₂O₃ and Gr remained in every stages. In (a) the reduction from Fe₂O₃ to FeO started and in (b) the reduction from FeO to Fe has progressed. In (c), as shown in Fig. 7(a), 0.503 g of pig iron grains were produced and 1.549 g of powder containing Fe₃O₄, FeO, and Gr remained.

The products after reaction were pig iron with a diameter of about 10 mm. The carbon concentration in pig iron was, as shown in Table 3, 0.1 mass% or less for A-3 and A-4, and in the hypo-eutectic composition of pig iron for B-2 and B-3. The carbon concentration of other pig iron was more than 5 mass% which included Gr powder.

In A-1 and A-2, the unreacted Gr was remained on the surface, but in A-3 and A-4, there was a little Gr on the surface and no Gr, respectively, as shown in Figs. 7(b) and 7(c). This is because most of the carbon was converted to CO gas and CO₂ gas.

In Series B, the smaller the particle size of Fe₃O₄ was, the less the amount of unreacted carbon remained.

In Series C, the longer the milling time was, the finer the graphite grains were crushed and the closer the Fe₃O₄ and Gr grains adhered, as shown in Fig. 8.
4. Discussions

4.1. Accuracy of Gas Analysis

The amount of mass loss due to the carbothermic reduction of Fe_3O_4 by microwave irradiation was compared with the mass of carbon and oxygen contained in CO and CO_2 in total product gas and the mass calculated from Eq. (3), as shown in Table 3. It can be also calculated from the component analysis of gas collected each reaction time, and its accuracy can be verified.

The total flow rate of the gas after reaction is \( \int_{0}^{\infty} N_2 \frac{100}{(N_2 \%)}, \)

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|c|c|c|c|c|c|}
\hline
sample & Pig iron and Mass decrease & Total produced Gas & Calculated from Eq. (3) \\
No. & Initial/g & %C & Decrease/g & Volume/l & CO% & CO_2% & (CO+CO_2)/g & mass% & (CO+CO_2)/g & mass% \\
\hline
A-3 & 3.0025 & 0.097 & 1.1212 & 1.73 & 40.66 & 9.32 & 1.12 & 100 & 1.10 & 98 \\
A-4 & 3.0024 & 0.069 & 0.9744 & 1.69 & 35.11 & 9.74 & 1.04 & 107 & 0.95 & 97 \\
B-1 & 3.0033 & 7.01 & 1.1927 & 1.90 & 49.3 & 6.25 & 1.12 & 100 & 0.93 & 75 \\
B-2 & 3.0018 & 3.6 & 1.1237 & 1.90 & 49.78 & 4.69 & 1.21 & 100 & 1.16 & 96 \\
B-3 & 3.0043 & 4.15 & 1.2047 & 1.54 & 44.05 & 8.76 & 1.19 & 100 & 1.20 & 100 \\
C-1 & 3.0033 & 7.01 & 1.1237 & 1.90 & 49.3 & 6.25 & 1.12 & 100 & 1.16 & 96 \\
C-2 & 3.0024 & 7.84 & 1.1202 & 1.90 & 49.78 & 4.69 & 1.21 & 100 & 1.16 & 96 \\
C-3 & 3.0006 & 9.52 & 1.1102 & 1.94 & 44.27 & 7.33 & 1.24 & 112 & 1.04 & 94 \\
\hline
\end{tabular}
\caption{Mass decrease by carbothermic reduction of Fe_3O_4 and graphite comparing with the mass of CO and CO_2 in total product gas and the mass calculated from Eq. (3).}
\end{table}

\( (CO\%) + (CO_2\%) + (N_2\%) = 100 \) \hspace{1cm} B-1 and C-1 are the same sample.
where \( f_{N_2} \) is the flow rate of \( N_2 \) gas and 100 ml/min. The production rates of \( CO \) gas and \( CO_2 \) gas are expressed by the following equations, respectively.

\[
\frac{dn_{CO}}{dt} = \frac{P_T}{RT} f_{N_2} \frac{(CO\%)}{(N_2\%)} 
\]

\[
\frac{dn_{CO_2}}{dt} = \frac{P_T}{RT} f_{N_2} \frac{(CO_2\%)}{(N_2\%)} 
\]

where \( n_i \) is the number of moles of \( i \) gas, \( P_T \) is atmospheric pressure, \( T \) is room temperature (280 K), and \( R \) is the Gas constant. The total mass loss, \( \Delta m \), can be calculated by the following equation.

\[
\Delta m = \frac{P_T}{RT} \left[ \int_0^t \left( M_{CO} \frac{(CO\%)}{(N_2\%)} + M_{CO_2} \frac{(CO_2\%)}{(N_2\%)} \right) dt \right] 
\]

where \( t \) is time of measurement and \( M_i \) is the molecular weight of \( i \)-gas.

Table 3 shows the results by the graphical integration using the data of Figs. 3 to 5. The results agree with the amount of mass loss in the range of 92% to 100% except the result of B-2 which is 75%, but the reason of the disagreement is unknown.

4.2. Determination of Major Chemical Reactions

The carbothermic reduction of \( Fe_3O_4 \) is represented by the following Eqs. (4) to (10), and in these reactions the independent reactions are 3 due to the phase rule.

\[
Fe_3O_4 + CO \rightarrow 3FeO + CO_2
\]

\[
FeO + CO \rightarrow Fe + CO_2
\]

\[
C + CO_2 \rightarrow 2CO
\]

Equation (6) is the Boudouard reaction. Also, in the direct reduction with C, there are

\[
Fe_3O_4 + C \rightarrow 3FeO + CO
\]

\[
Fe_3O_4 + (1/2)C \rightarrow 3FeO + (1/2)CO_2
\]

\[
FeO + C \rightarrow Fe + CO
\]

\[
FeO + (1/2)C \rightarrow Fe + (1/2)CO_2
\]
The Gibbs energy changes of these reactions, $\Delta G$, is expressed by the following equation.

$$\Delta G = \Delta G^0 + RT\ln K \tag{11}$$

where $\Delta G^0$ is the standard Gibbs energy change of reaction, and $K$ is represented by the partial pressures of CO and CO$_2$ gases when the reactant and the product are pure substances.

I. Prigoine et al.\textsuperscript{22} defined the entropy production, $\Delta S$, by the following equation and quantitatively applied it to the thermodynamics under non-equilibrium state.

$$\Delta S = \Delta S + \Delta S \tag{12}$$

where $\Delta S$ is the entropy change of system and $\Delta S$ is the entropy flow. From the second law of thermodynamics, the entropy production must be always positive.

$$\Delta S \geq 0 \quad (\text{is in equilibrium}) \tag{13}$$

Using Eq. (12), the Gibbs energy change of reaction under constant pressure is expressed by the following equation.

$$\Delta G + \Delta S\Delta T - \Delta X_m = -Td\Delta S < 0 \tag{14}$$

where $X_m$ is the energy generated in materials by absorbing microwave and takes positive value. $X_m$ is consumed for the entropy change of system, the energy of chemical reaction and the uncompensated heat, $Td\Delta S$.

$\Delta S$ can be approximated with the standard entropy change of reaction, $\Delta S^0$. $\Delta G$ and $\Delta S$ are quantity of state. $X_m$ and $\Delta S$ are not quantity of state and depend on reaction process and reaction time, $\Delta t$. The integration of Eq. (14) from 0 to $\Delta t$ gives the following equation,

$$\Delta G + \Delta S^0\Delta T = -T\Delta S + X_m \tag{15}$$

where $\Delta T = \int_0^{\Delta t} \left(\frac{dT}{dt}\right) dt$ and $\int_0^{\Delta t} \frac{dT}{dt}$ is the rate of temperature rise.

The closer $\Delta G$ becomes to 0, the nearer the state of reaction to equilibrium is, and the reaction dominates in the system. Under microwave irradiation, $\Delta G < 0$ and the reaction proceeds to the right side of reaction equation. After the reaction ends, $\Delta G = T\Delta S = 0$ but $X_m > 0$. Carbon powder is heated by microwave. When microwave irradiation is stopped, the reaction stops and $X_m = \Delta T = \Delta G = \Delta S = 0$.

When $\Delta t = 1$ s, the value of $\Delta G + \Delta S^0\Delta T$ for each reaction of Eqs. (4) to (10) can be obtained using each experimental data. Figure 9 shows the results for A-I which is a typical tendency. In the stage II, the rate of temperature rise becomes small, and the magnitude of the value of $\Delta S^0\Delta T$ is about several% of the total, and in the stage III, it is 1% or less.

In the stage I, temperature reaches maximum at 1 100°C in 37 s, the value of $\Delta G + \Delta S^0\Delta T$ for the reaction of Eq. (5) is near zero, but no reaction occurs as mentioned in the chapter 4.3. At temperature of 627°C in 44 s, as the value for the reaction in Eq. (4) is negative and near zero, the reduction of Fe$_3$O$_4$ to FeO by CO gas proceeds, but Eq. (6) does not occur.

Subsequently, after 66 s at the end of the stage II and the start of the stage III, the values of $\Delta G + \Delta S^0\Delta T$ for the reactions of Eqs. (4) to (10) are all negative, and the value of Eq. (4) is closest to 0. The Boudouard reaction of Eq. (6) dominates for supplying CO gas. The same tendency was shown for other samples.

The net reaction equation of Eqs. (4) to (6) is expressed by the following equations.

$$\frac{1}{3}\text{Fe}_3\text{O}_4(s) + \frac{2}{3}\text{CO}(g) \rightarrow \frac{1}{3}\text{Fe}_2\text{O}_3(s) + \text{CO}_2(g) \tag{16}$$

where $n = \frac{p_{\text{CO}}}{p_{\text{CO}} + p_{\text{CO}_2}}$. Taking into account that $\Delta S^0$ is almost independent on temperature and using the relationship of $G = H - TS$, the enthalpy change of reaction, $\Delta H$, for the net reaction is expressed by the following equation.

$$\Delta H - X_m = -T\Delta S < 0 \tag{17}$$

$X_m$ is the energy generated per 1 mol of Fe by absorbing microwave. $\Delta H$ for heating a mixture of Fe$_3$O$_4$ and C from 25°C to 1 400°C and producing pig iron is expressed by the following equation.\textsuperscript{25}

$$\Delta H = 471.535 - \frac{491.464(1 - 0.7585n)}{(2 - n)} \quad (\text{kJ} / \text{mol} \cdot \text{Fe}) \tag{18}$$

When $n = 1$, $\Delta H$ is endothermic and 352.8 kJ/mol (that is, 6 369 kJ/kg-Fe = 1.77 kWh/kg-Fe), where the heat of solution of carbon to molten pig iron is assumed to be negligible small.

In the present experiment, the weight of pig iron was about 1.9 g, so $\Delta H = 3.36$ WH. On the other hand, the microwave power was 2.8 kW and 156 WH was supplied into the furnace for 200 s. Therefore, the utilization efficiency of microwave is apparently 2%. Most microwave are reflected to the generator or absorbed by the wall of microwave furnace and dissipated to outside as heat.

The energy $X_m$ generated in Fe$_3$O$_4$ and Gr by absorbing microwave is consumed for heating the materials, proceeding the reaction and generating the entropy production.

4.3. Entropy Production

Since the reactions of Eqs. (4) and (5) have the same meaning as that one atom of oxygen is removed from iron
oxide, it can be expressed by the following equation.

\[ \text{O(in FeO}_3\text{)} + \text{CO} \rightarrow \text{CO}_2 \]  

The removing rate of oxygen is expressed using Eqs. (1) and (2).

\[ \frac{dn_O}{dt} = \frac{dn_{CO}}{dt} + 2 \frac{dn_{CO}}{dt} \]  

The reaction rate of carbon in Eq. (6) is expressed,

\[ \frac{dn_c}{dt} = \frac{dn_{CO}}{dt} + \frac{dn_{CO}}{dt} \]  

The entropy production by carbothermic reduction of Fe₃O₄ is expressed by

\[ T \frac{d\Delta S}{dt} = (A_O \frac{dn_O}{dt} + A_C \frac{dn_C}{dt}) \]  

where \( A_O = -\Delta G_O \) and \( A_C = -\Delta G_C \). \( A_O \) and \( A_C \) and \( A_G_O \) are the affinity and the Gibbs energy change of reaction, respectively, where \( A_O \) and \( A_G_O \) are for Eq. (4) in the stage I and Eq. (5) in the stage II and III and \( A_C \) and \( A_G_C \) are for Eq. (6) in all stages.

**Figure 10** shows the entropy production rate, \( T(d\Delta S/dt) \), and \( \Delta G + \Delta S^0\Delta T \) of Eq. (4) for the Stage I and Eq. (5) for the Stage II.

When temperature at the end of the stage I drops temporarily, the value of \( T(d\Delta S/dt) \) is 0 and no reaction proceeds though \( A_O \) and \( A_C \) are positive. The value of \( T(d\Delta S/dt) \) reaches maximum near 100 s when the reaction is most active. After that, it attenuates toward the end of the reaction and becomes 0. \( \Delta G \) also goes to 0. The same tendency was shown for other samples.

### 4.4. Activation Energy and Frequency Factor of Reaction Rate

Most of the carbothermic reduction of Fe₃O₄ by microwave heating proceeds within the short time of about 50 s from the end of stage I to stage II. K. Ishizaki et al. studied the carbothermic reduction of Fe₃O₄ in a carbon-composite pellet with microwave at 2.45 GHz in N₂ gas and showed that the reduction of FeO occurred near the contact between carbon and FeO particles. This indicates that the reaction rate is controlled by chemical reaction but not diffusion of elements. In this session, the effects of microwave on the activation energy and the pre-exponential factor of chemical reaction are discussed.

The reaction rate constant is expressed by the product of the frequency factor \( k^0 \) and the Boltzmann distribution of the rate, \( \exp (-E/RT) \). \( E \) is the activation energy, which is the energy gap between the initial and active state of reactant. Furthermore, energy is released when proceeding from the active state to the state of product. The difference of the energy gaps is the Gibbs energy change of reaction, \( \Delta G \). Therefore, the magnitude of \( E \) does not affect \( \Delta G \), which is the state function.

Ignoring the reverse reaction, the reaction rate of Eq. (19) is expressed as

\[ \frac{dn_O}{dt} = S_1k_1pcO(n^0_O - n_O) \]  

and the reaction rate of Eq. (6) is as

\[ \frac{dn_c}{dt} = S_6k_6pC_0(n^0_C - n_C) \]  

respectively, where \( S_6 \) and \( S_1 \) are the cross-sectional area of the reaction of Eqs. (6) and (19), respectively. The reaction rate constants, \( k_1 \) and \( k_6 \), are represented by

\[ k_1 = k^0_1 \exp \left( - \frac{E_0}{RT} \right) \]  

and

\[ k_6 = k^0_6 \exp \left( - \frac{E_C}{RT} \right) \]  

Logarithms of both sides of Eqs. (23) and (24) are obtained.

**Figures 11** and **12** show plots of Eq. (27) for the reduction of iron oxide and the Boudouard reaction for each sample, respectively. The horizontal axis in the figure is \( 1/T \) (K) and the vertical axis is \( \log(Sk^0) \). \( n^0_O \) and \( n^0_C \) are total moles of oxygen and carbon in exhaust gas, respectively, and are obtained by graphical integration on Figs. 3 to 5 using Eqs. (1), (2), Eqs. (20) and (21).

All plots show complex behavior. In the stage II, Eq. (27) changes almost linearly, and the apparent activation energy can be obtained from the slope in the latter half of the stage. Each component in sample has different temperature due to the different electromagnetic property and the shape. Therefore, temperature is locally different. M. Hayashi et al. heated 1 g of Fe₃O₄ powder (about 1 μm diameter and 38.6% of relative bulk density) using single mode microwave at 2.45 GHz with 0.1 kW. Temperature reached at 585°C of the Curie point in 10 s to be in steady state and after then rose to 800°C in 50 s to be in steady state. This evidence showed that temperature in the sample became uniform. In the present experiments. When temperature rose above 800°C in the stage II and the stage III, the heat generated inside the sample rapidly transfers between
particles as radiant heat, and temperature became close to the uniform temperature. This tendency is remarkable for powder sample.

The results are shown in Table 4. The apparent activation energy of reduction of iron oxide in each sample is 4 kJ/mol to 55 kJ/mol, and the apparent activation energy of the Boudouard reaction is 32 kJ/mol to 103 kJ/mol. Obviously, the apparent activation energy of the reduction of iron oxide is smaller than the Boudouard reaction.

I. Seki et al. 23) measured the rate of carbothermic reduction of Fe_2O_3 in-situ using a high-temperature X-ray diffractometer. They obtained the apparent activation energy of reduction from Fe_3O_4 to FeO to be 113 kJ/mol to 231 kJ/mol and that from FeO to Fe to be 81 kJ/mol to 103 kJ/mol. The value in the present experiment is obviously smaller than that by I. Seki et al.

The Gibbs energy change ΔG^o of the reaction from the initial state to the activated state of reactant is equal to the activation energy E. The reaction rate is proportional to the probability of creating activated state, exp (ΔS^o/R). Assuming that the initial and activated states of reactant are in

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Activation energy (kJ/mol)</th>
<th>Increase ratio of pre-exponential factor for 1 s at 1200°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-1</td>
<td>4.3</td>
<td>1.03</td>
</tr>
<tr>
<td>A-2</td>
<td>14</td>
<td>1.03</td>
</tr>
<tr>
<td>A-3</td>
<td>35.4</td>
<td>1.04</td>
</tr>
<tr>
<td>A-4</td>
<td>38.6</td>
<td>1.04</td>
</tr>
<tr>
<td>B-1</td>
<td>52.6</td>
<td>1.05</td>
</tr>
<tr>
<td>B-2</td>
<td>67.5</td>
<td>1.05</td>
</tr>
<tr>
<td>B-3</td>
<td>54.8</td>
<td>1.05</td>
</tr>
<tr>
<td>C-1</td>
<td>52.6</td>
<td>1.05</td>
</tr>
<tr>
<td>C-2</td>
<td>17.9</td>
<td>1.04</td>
</tr>
<tr>
<td>C-3</td>
<td>19.2</td>
<td>1.05</td>
</tr>
</tbody>
</table>

E_0 and E_c are for O (in FeO)+CO→CO_2 and C+CO_2→2CO, respectively, during the late of the stage II. The increase ratio of pre-exponential factor for 1 s at 1200°C is in the beginning of the stage III.
equilibrium, \(- T\Delta S^\circ = \Delta G^\circ - X_m\). Therefore, the following equation is obtained.

\[
k = k^0 \exp \left( - \frac{E - X_m}{RT} \right) \quad \text{...................(28)}
\]

where \(X_m\) is energy generated per 1 mol of the sample. The weight of sample was about 0.06 mol. The microwave power was 2.8 kW, but the absorption efficiency was 2%. Then, \(X_m\) was about 1 kJ/s·mol. Since the irradiation time of microwave until the end of the stage II was about 100 s, \(X_m = 50 \text{ kJ/mol}\).

On the other hand, in the early stage of the stage III, pig iron was produced with luminescence, and the Sk value increased rapidly at the vicinity of 1 200°C to 1 400°C. In the stage I, the rapid temperature rise was caused by the magnetic loss of \(\text{Fe}_3\text{O}_4\) and the induced current by Gr, and reached to near 1 100°C which was higher than 585°C of the Curie point of \(\text{Fe}_3\text{O}_4\). Then, \(\text{Fe}_3\text{O}_4\) reduced to \(\text{FeO}\) in a few second.

K. Hara et al.\(^2\) proposed the following excited species in the end of the stage II to the beginning of the stage III,

\[
\text{Fe}^{2+} + 2e \rightarrow \text{Fe}^* \quad \text{(excited)} \quad \text{.............(29)}
\]

\[
\text{Fe}^* \rightarrow \text{Fe}^0 \quad \text{(ground state)} - \hbar \nu \quad \text{...........(30)}
\]

where \(\nu\) is the wave number of light emitted when Fe falls from the excited state to the ground state. \(\hbar\) is the Planck’s constant. The electrons in carbon could be also activated by microwave and contribute to the activation energy of the Boudouard reaction.

\[
C \rightarrow C^* \quad \text{(excited electron)} \quad \text{................(31)}
\]

\[
C^* + \text{CO}_2 \rightarrow 2\text{CO} \quad \text{...................(32)}
\]

The value of Sk from 100 s to 150 s in each sample are calculated at the normalized temperature of 1 200°C using the apparent activation energy in the stage II. The increasing rate of \(k\) per 1 s is calculated assuming that \(S\) is constant. As shown in Table 4, it increases by 3%/s to 5%/s for the reduction of iron oxide and 4%/s to 10%/s for the Boudouard reaction, except B-2.

These phenomena show that microwave contributes to the increase of kinetic energy of electrons related to the reaction, and the effect appears in the frequency factor \(k\). When the energy \(W_m\Delta t\) generated by microwave is added to the thermal vibration energy RT, the reaction rate constant \(k\) can be expressed as

\[
k = k^0 \left( 1 + \frac{W_m\Delta t}{nRT} \right) \exp \left( - \frac{E - X_m}{RT} \right) \quad \text{...................(33)}
\]

where \(n\) is the mol of sample and about 0.06 mol. \(W_m\) is 56 W, considering 2% of the absorption efficiency of microwave power of 2.8 kW. RT at 1 200°C is 12.2 kJ/mol. Thus, \(\frac{W_m}{nRT}\) is about 8%/s. The energy generated by microwave absorption is stored as the kinetic energy of electrons in the reactant and accelerates the reaction rate. Light emission was observed in the beginning of the stage III in accordance with Eqs. (29) and (30), followed by producing molten pig iron.

These assumptions should be discussed more using a simple reaction system such as carbothermic reduction of NiO.\(^{24}\)

4.5. Effect of Contact State of Materials on \(E\) and \(k\)

In the carbothermic reduction of \(\text{Fe}_3\text{O}_4\) by microwave irradiation, the value of Sk is always larger for the Boudouard reaction than the reduction of \(\text{Fe}_3\text{O}_4\) or \(\text{FeO}\). This indicates that the Boudouard reaction is preferentially promoted by microwave near the contact points between Gr particles. In the stage I, the pre-exponential factor of reaction rate increases due to the magnetic loss, and the reduction rate from \(\text{Fe}_3\text{O}_4\) to \(\text{FeO}\) increased. In the subsequent stage II, the apparent activation energy of reaction rate by microwave heating was lower than that by conventional heating, and in the stage III, the pre-exponential factor of reaction rate increased due to the induction current loss in \(\text{FeO}\) and Gr particles, and the reduction from \(\text{FeO}\) to Fe and the production of molten pig iron are promoted.

Figure 13 shows the influence of the contact of materials on these phenomena. The mixing ratio of \(\text{Fe}_3\text{O}_4\) and Gr in Series A, the size of \(\text{Fe}_3\text{O}_4\) particles in Series B and the milling time of \(\text{Fe}_3\text{O}_4\) and Gr in Series C were changed, respectively. These sample treatments changed the amount of contact points between Gr and \(\text{Fe}_3\text{O}_4\) particles. The smaller the proportion of Gr in Series A, the larger the particle size of \(\text{Fe}_3\text{O}_4\) in Series B and the shorter the milling time in Series C were, the smaller the amount of contact points became. The value of B-2 is a reference value because of uncertain temperature measurement.

\(\Delta G + \Delta S^\circ\Delta T\) is the quantity of state, and the effect of

\[\text{Fig. 13. Effect of sample treatments on } \Delta G + \Delta S^\circ\text{, the apparent activation energy and the increase rate of pre-exponential factor of reaction rate of the reaction of } \text{FeO+CO} \rightarrow \text{Fe+CO}_2, \text{Fe}_2\text{O}_3+\text{CO} \rightarrow 3\text{FeO+CO}_2 \text{ and the Boudouard reaction: } \Delta G + \Delta S^\circ\text{ is the mean value between 70 to 100 s. (Online version in color.)}\]
sample preparation on this value is related to temperature and \( P_{\text{CO}} \) and \( P_{\text{CO}_2} \). In Series A, when the amount of Gr decreased with decreasing the contact points of Gr particles, CO gas produced by the Boudouard reaction decreased. \( P_{\text{CO}} \) decreased, so \( \Delta G \) increased. In Series B, the diameter of the \( \text{Fe}_3\text{O}_4 \) particle increased and the contact points with Gr decreased, so \( P_{\text{CO}_2} \) decreased and \( \Delta G \) increased negatively. In Series C, milling causes Gr particles to become fine, and the contact points between Gr particles increased. Therefore, \( \Delta G \) increased negatively.

The apparent activation energy decreased with increasing the amount of contact points between FeO and Gr particles. Near the contact point of the particles, the intensity of the electromagnetic field of microwave tends to increase, and temperature and reaction rate increase locally. At lower temperature reactions are locally promoted because of less radiant heat transfer. Therefore, the apparent activation energy of reaction by microwave irradiation is lower than conventional heating. Since \( X_m \) is proportional to the amount of contact points, the value of \( E - X \) became.

\[
X_m = \frac{E - X}{n}
\]

As mentioned in Section 4.4, the frequency factor depends on the kinetic energy of electron and is not related to the amount of contact points.

5. Conclusions

The carbothermic reduction of \( \text{Fe}_3\text{O}_4 \) was carried out by microwave irradiation, and the concentration of CO and \( \text{CO}_2 \) gas in exhaust gas were measured. From the concentration of each gas, the reaction rates of iron oxide reduction and the Boudouard reaction were calculated as well as the Gibbs energy change of reaction, \( \Delta G \), and the entropy production, \( \Delta S \). Also, the pre-exponential factor of reaction rate constant and the apparent activation energy of reaction were obtained.

The reaction was divided into three stages. In the stage I, temperature rose sharply due to the magnetic loss of \( \text{Fe}_3\text{O}_4 \) and the heat generated in Gr by induction current loss, and \( \text{Fe}_3\text{O}_4 \) was rapidly reduced to FeO. The pre-exponential factor of reaction rate constant increased. In the stage II, the reduction from FeO to Fe occurred, and the apparent activation energy of reaction rate became smaller than conventional heating. In the stage III, heat was generated by induction current loss in Gr particles, and the pre-exponential factor of reaction rate constant increased.

The amount of contact points between \( \text{Fe}_3\text{O}_4 \) and Gr particles was changed by the composition of Gr powder, the diameter of \( \text{Fe}_3\text{O}_4 \) particles and milling time. The reaction rate constant was always larger for the Boudouard reaction than the reduction of \( \text{Fe}_3\text{O}_4 \) or FeO. This indicates that the Boudouard reaction is preferentially promoted by microwave near the contact points between Gr particles.

The larger the amount of contact points of Gr and \( \text{Fe}_3\text{O}_4 \) particles was, the more negative \( \Delta G \) became. The apparent activation energy decreased with increasing the amount of contact points, but the increase rate in the frequency factor did not change.

REFERENCES