Pig iron making by microwave heating

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ABSTRACT

Magnetite ore powder mixed with 18 mass% of graphite, coke or coal was heated by microwave with 2.45GHz under nitrogen gas. The mixed powder was heated up to 1360℃ during 10 min and pig iron with 3 to 4 mass% of carbon was produced. During the reduction of iron oxide, CO and CO_2 gases generated. Their concentrations were analyzed using a gas chromatography and the weight loss of the mixture was measured using a thermal balance. The reduction proceeded in 2 steps of first 100s and after. In the first step, the temperature rapidly increased up to about 800℃ and then decreased to about 600℃. CO_2 gas was produced more than CO gas. After 100s, the temperature gradually increased and CO gas was predominantly produced. In the first step, magnetite absorbed magnetic field energy of microwave to generate heat and was reduced to wustite (FeO). In second step, graphite in the mixture absorbed the electric field energy of microwave to generate heat. Many hot spots appeared in the mixture to generate heat during heating. Then the temperature of sample was apparently low.

KEYWORDS: magnetite, graphite, pig iron, microwave, gas chromatography, environments

INTRODUCTION

The decrease of CO_2 gas emission half until 2050 is very important problem for human in the world. The process of pig iron making in blast furnace consumes about 0.5t of coke per 1t of hot metal and produces about 1.8t of CO_2 gas. 125 million tons of crude steel was produced in Japan in 2007 and 13% of total CO_2 gas emission in Japan was emitted from ironmaking processes. Carbon consumed for making pig iron from iron ore is composed of 2 parts; one is from the mass balance for deoxidizing iron oxide to produce pig iron and the second is for burning to make energy such as high temperature gas in order to heat resources and promote the reduction of iron ore. The first consumption of carbon is 225kg of coke and the second is 275kg. When the energy obtained from the second carbon is replaced to microwave energy, almost half of CO_2 gas emission from pig iron making is reduced. In a blast furnace, it is very important to permeate high temperature gas through resources for supplying energy and it is necessary to use hard lump iron ore and coke with walnut size. Then, it takes 6 to 8 hrs to produce pig iron from iron ore. As fine powder has large surface area relative to its volume, it is expected that iron ore powder can be rapidly reduced with carbon. In blast furnace, it is impossible to use powder iron ore because of flying powder and clogging the channel among iron ore and coke. The reverberator and the electric arc furnace are used for melting metals by infrared light with short wave length of about 1 μm. Infrared light reflects on the surface of materials and it is impossible to heat behind solid materials. The wavelength of microwave is longer than infrared light and microwave also reflects on the surface. However, microwave can penetrate through powder materials to heat them from the inside. By microwave heating, the mixed powder of iron ore and graphite can make the reduction of iron ore rapid to produce pig iron. This indicates the possibility of the construction of compact furnace for making pig iron.

The feasibility of the pig iron making process by microwave heating has been studied. The reduction of magnetite by carbon to pig iron with 3 mass% of carbon at 1350℃ requires the energy of 4.1MJ per 1 ton of hot metal, where the out gas of CO-50%CO$_2$ at 500℃ is produced and the efficiency of energy transfer from electricity to molten pig iron is 64%. The required energy corresponds to the electricity of 1150kWH and the cost of electricity is about 8,000 yen under the assumption of the average cost of 7 yen per 1 kWH in day and night. In the spring of 2008, the cost of coke increased triple to 300$ from 100$ per 1 ton. The energy cost for making pig iron in blast furnace is about 24,000 yen per 1 ton of hot metal.

The reaction in the mixed powder of iron ore and carbon proceeded at many hot spots in the mixture and the mean temperature has been measured to be lower than temperature at the reaction sites[1-3]. In the present paper, the reduction rate of magnetite powder mixed with carbon heated by microwave was measured using a gas chromatography and the kinetics was discussed.

EXPERIMENTAL

Spherical composite pellets with about 20 mm diameter were prepared using a pelletizer from a mixture of magnetite ore (named Romeral) (*ca*. 50 μm diameter), coal (named Robe River) (*ca*. 40 μm diameter) and 2 mass% of bentonite powder as a binder. The amount of coal was determined by taking into account the amount of carbon required for reducing iron ore completely to form 87%CO+13% CO$_2$ gas and for producing pig iron with 2 mass% of carbon. The weight of the pellets is about 8 g.

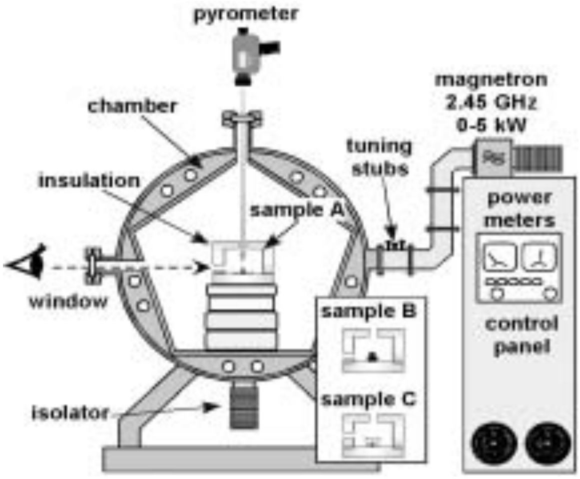


Fig.1 Microwave furnace with 5kW for making pig iron

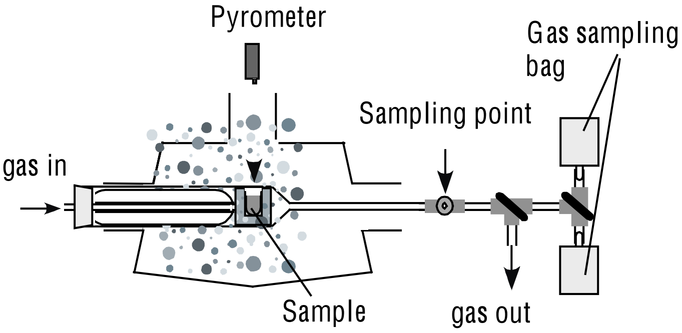
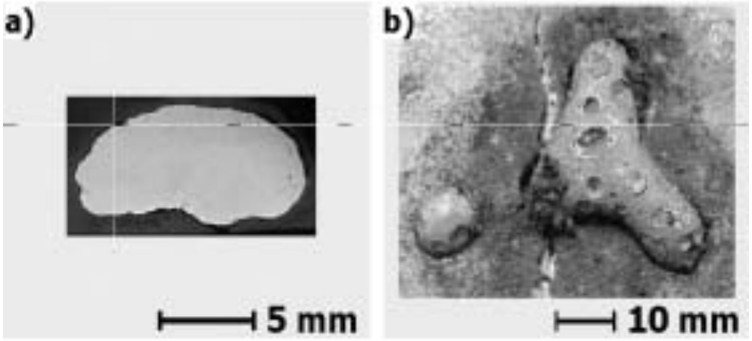


Fig. 2 Reaction tube in a microwave furnace and gas sampling system

A microwave generator with 5kW maximum power at 2.45 GHz was employed, as shown in Fig.1. As the shape of the microwave oven chamber is pentagon, the electric field (E-field) and the magnetic field (H-field) modes of microwave could be mixed. One or four pellets were set in the middle of the microwave oven chamber and covered with an alumina insulator. Silicon carbide as an exothermic auxiliary substance was pasted inside of the alumina insulator to heat it and compensate the heat lost from the pellet.

Magnetite powder (Fe_3O_4) with the mean diameter of 1 μm and the purity of 99% and graphite powder with 75 μm and 99% were mixed in a stainless mortar. The mixture ratio of Fe_3O_4 to C was 81.37 : 18.63 mass%. The mixture of 1.82g was put in a alumina crucible and set in a silica tube in a microwave furnace as shown in Fig.2. The alumina crucible was surrounded using porous alumina bricks. Dead volume in upper stream of gas was diminished using a silica core. The product gas was led out through a fine silica tube. The frequency of microwave was 2.45 GHz and the maximum power of the furnace was 2.8kW. The shape of the furnace chamber was pentagonal rather than square for mixing the electric and magnetic modes of microwave, as shown in Fig.2. The temperature of the sample surface was measured using a 2-color pyrometer. Nitrogen gas with the purity of 99.9995% was passed through the silica tube with the rate of 100 ml/min and the microwave of 2.8kW was supplied. The product gas of about 2 ml was sampled at the sampling point, as shown in Fig.2, every 30s during first 3 min and every 1 min during 3 to 10 min. The total product gas was collected in some gas sampling bags. The product gases were analyzed using a gas chromatography. The sample powder and the product powder were analyzed using a X-ray diffractometer. The concentration of carbon in pig iron was measured using a LECO and those of the other elements were measured using a XRF.



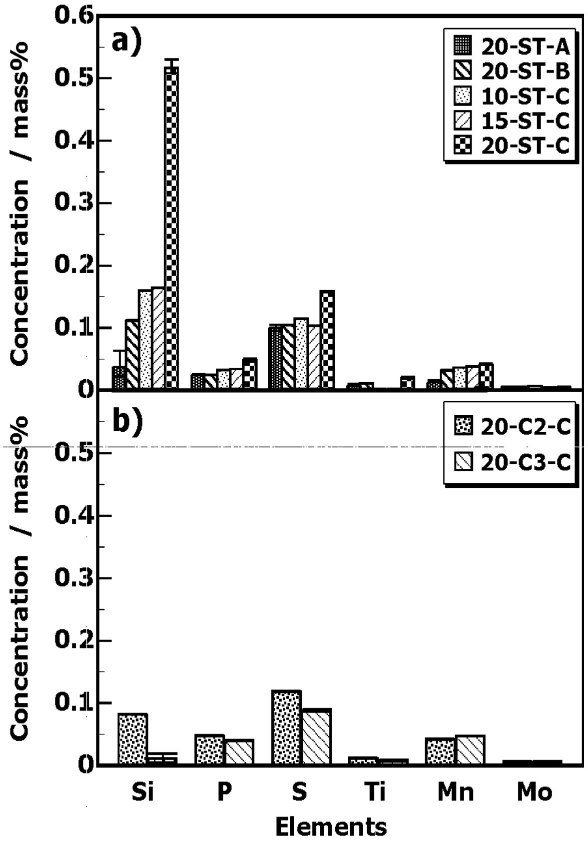


Fig.6 Impurities in pig iron

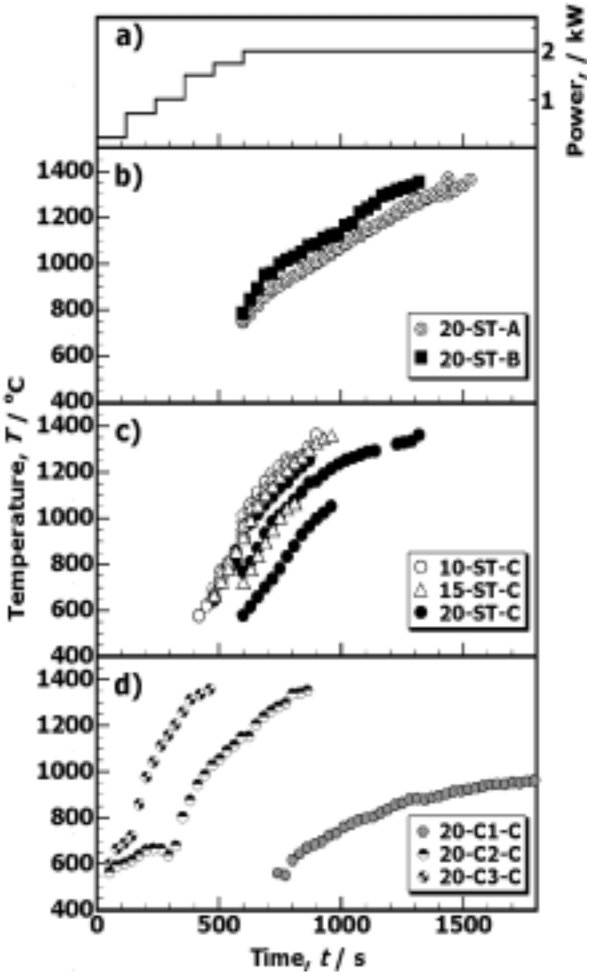


Fig.4 Temperature increase of pellets: (b)A is one pellet with 20 mm ϕ, B is four, (c)one pellet with 10, 15 and 20 mm ϕ and (d)one pellet with 20mm ϕ under 1kW(C1), 2kW(C2) and 3kW(C3)

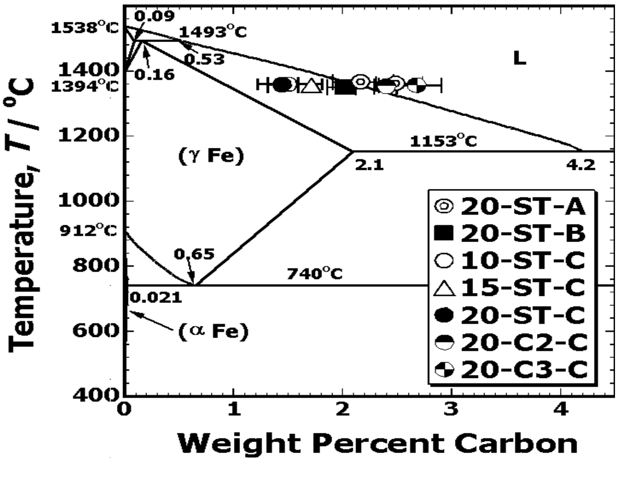


Fig.5 Carbon content in pig iron

RESULTS

After the start of heating, the inside of alumina insulator brightened and pellet was clearly observed. Soon, soot came out of pellet and ceased. During the step-up of microwave power, a yellow flame was generated from pellet during heating, pellet gradually brightened in red to yellow. When the temperature of pellet attained at about 1350°C, pellet melted down to be pig iron and disappeared from the view. On the surface of pig iron in pebble slag was partially adhered, as shown in Fig. 3 b) and Fig. 4. From the cross section of pig iron pebble, slag and gang materials did not included in pig iron, as shown in Fig. 3 a).

Fig. 4(b) shows the time

–temperature profiles of one and four pellets heated by the step power supply without crucible. Fig. 4(c) shows the profiles of pellets with 10, 15 and 20 mm diameter heated in an alumina crucible by the step power supply. The pellet size does not seem to affect the temperature increase rate. On the other hand t he temperature increase rate for pellets with 20 mm diameter heated under constant power increased with increasing microwave power, as shown in Fig. 4(d). 1 kW power was not enough to heat a pellet with 20 mm diameter up to the temperature for producing pig iron. In the case of 2 and 3 kW power supplies, the pellets heated very rapidly up to approximately 600°C.

The carbon concentration of pig iron is plotted in the Fe-C phase diagram of Fig. 5. The carbon concentrations of pig iron from one pellet heated by the step power supply in an alumina crucible are in the coexisting phase of solid and liquid and by constant power supply in the liquid phase near the liquidus-line. In the case of one and four pellets heated by the step power supply without alumina crucible the carbon concentrations are on the liquidus-line.

The impurities in pig iron are shown in Fig. 6 a) and b) for the step and constant power supplies, respectively. Pig irons from pellets placed in a crucible and heated by the step power supply have higher concentration of impurities than those heated by constant power supply. The content of impurities in pig iron from one and four pellets heated without alumina crucible by the step power supply are slightly lower than those from pellets heated in an alumina crucible. Pig iron produced in faster heating contains lower content of impurities.

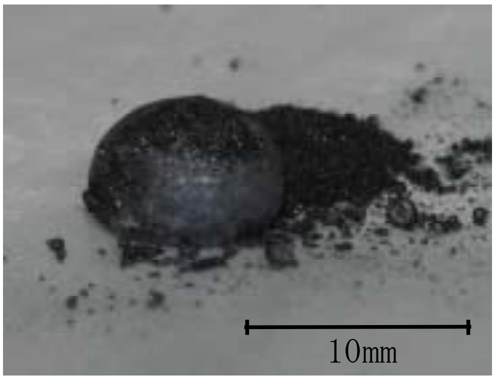


Fig. 7 Pig iron droplet produced from the mixture of magnetite and graphite powder heated by microwave

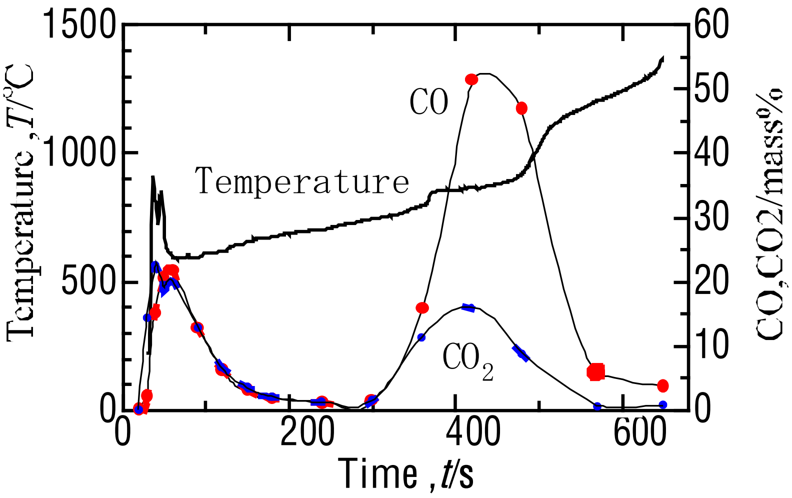


Fig. 8 Temperature change of the sample surface heated by microwave and the concentration of CO and CO_2 product gases in N_2 carrier gas

Fig. 7 shows the pig iron droplet of 1.01g produced in heating during 660 s. As shown in Fig. 8, the temperature of the sample surface sharply increased up to about 800℃ in the initial stage and decreased to about 600℃. In the second stage until 550s, the temperature gradually increased up to 900℃ and in the third stage until 660s, it rapidly increased up to 1360℃. Then pig iron was produced. The concentration of carbon in pig iron was 4.0494%.

The composition of CO_2 of product gas in N_2 carrier gas increased more rapidly than that of CO in the initial stage. Until 300 s in the second stage, the pro duct gases decreased to almost zero % and at more than 700℃, CO and CO_2 gases were actively produced. CO gas was produced by 3 times than CO_2 gas. According to preceding the reduction of iron ore, the composition of the product gases decreased. In the third stage, the reduction of iron ore already finished and the reduced iron absorbed carbon to be molten pig iron.

DISCUSSION

The reliability of gas analysis can be confirmed by the comparison of the measured weight decrease of sample to calculated one from CO and CO_2 compositions in produced gas.

$$\Delta m_t = \frac{f^0_{N_2}}{RT} P_T \int_0^t \left(M_{CO} \frac{x_{CO}}{x_{N_2}} + M_{CO_2} \frac{x_{CO_2}}{x_{N_2}} \right) dt$$

where f^0_{N2} is the flow rate of nitrogen gas, T is room temperature in absolute temperature, P_T is atmospheric pressure, M_i and X_i are molecular weight and mole fraction of gas molecule i, respectively. R is gas constant and t is the reaction time. The measured weight decrease of sample was 0.68g, while the calculated one was 0.65. The measured and calculated weight change agreed in the accuracy of 95.7%.

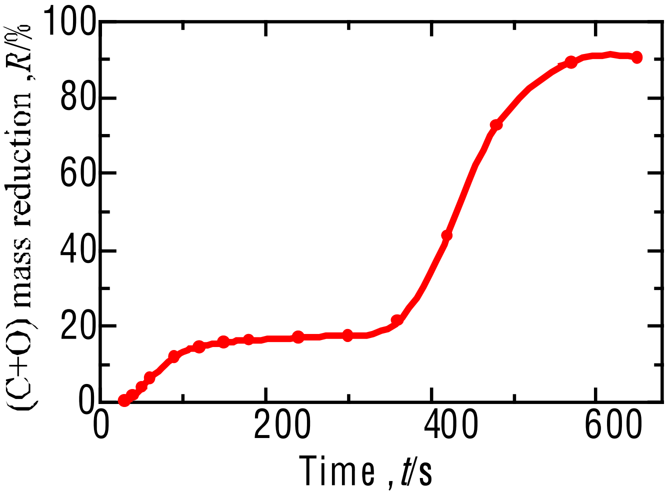


Fig. 9 Total weight change of oxygen and carbon in sample according to the reduction reaction measured by thermal balance.

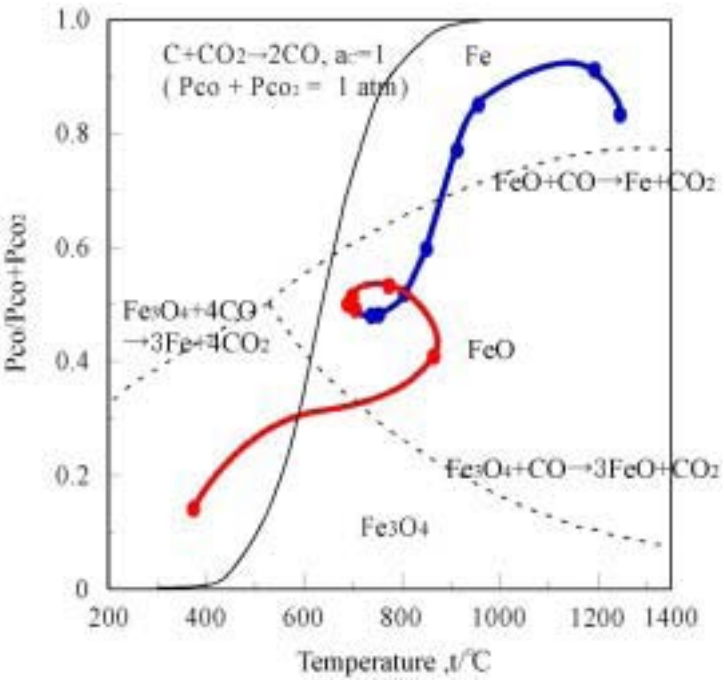
The weight change corresponds to the total weight change of oxygen in iron oxide and carbon according to the reduction reaction. As shown in Fig. 9, the total weight of sample decreased in the initial stage. In this stage, magnetite particles in the sample locally generated heat to make high temperature. The reduction of magnetite with carbon can be presented as

$$2Fe_3O_4 + C \rightarrow 6FeO + CO_2$$

$$Fe_3O_4 + C \rightarrow 3FeO + CO$$

The average reaction rate of the reduction of Fe_3O_4 to FeO was $1.3\text{x}10^{-3}$ g/s.

After then, in the second stage, the reaction stopped up to about 700 ℃ until 350s, because the temperature of sample was over the Currie point. Magnetite particles did not generate heat and the Boudour reaction did not proceed.



against temperature. The hatched line shows the stable areas of each iron oxide. The solid line shows

$$CO_2 + C \rightarrow CO_2$$

From 350s the carbon particles locally generated heat according to induction heating and the surface temperature of mixture again started to increase. Over about 700℃, the Boudour reaction proceeded and the reduction of wustite to iron took place.

$$FeO + CO \rightarrow Fe + CO_2$$

The weight of sample rapidly decreased and the reduction reaction proceeded until 550s. The average reaction rate of the reduction was $3.3\text{x}10^{-3}$g/s. After then molten pig iron was produced. The final % of reduction attained to 92% that caused from the error of gas chromatography.

The trace of $P_{CO}/(P_{CO}+P_{CO2})$ against the temperature of sample surface is shown in Fig. 9. In the initial stage, the temperature sharply increased and the weight of sample decreased. The trace at lower temperature moves in the area from Fe_3O_4 to FeO in phase diagram. The composition of CO gas in the product gas was higher than that by the Bourdour reaction in equilibrium and soon it became lower than that in equilibrium. In the second stage, the sample powder was in the stable area of FeO. Over 850℃ the sample entered in the stable area of Fe and FeO is reduced to Fe. In the third stage, FeO in the sample was completely reduced and the CO gas composition decreased.

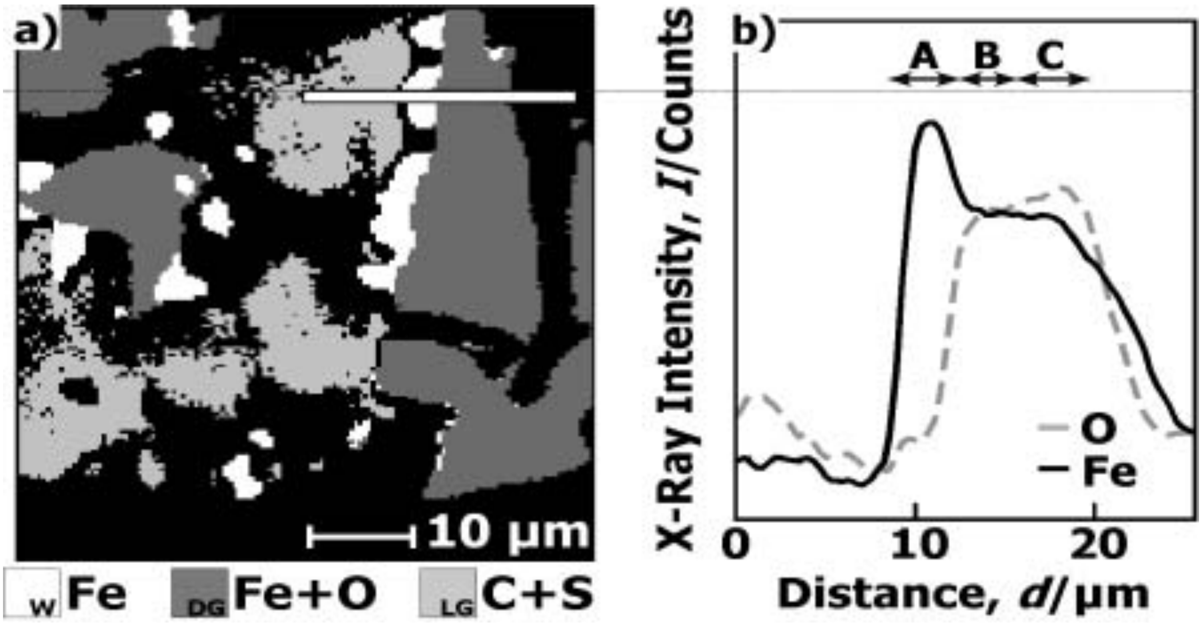


Fig.10 Reaction spots in a pellet. (a)Fe is reduced iron, Fe+O is wustite and C+S is carbon, (b) the concentration profiles of Fe and O in the white line in (a)

The BSE image of the cross section of the pellet of magnetite ore and coal heated up to 1050ºC is shown in Fig.10 (a). The concentration profiles of Fe and O are shown Fig.10 (b). These line profiles show 3 areas; A, B and C with different Fe and O intensities. Area A has a high intensity of iron and low oxygen. In B the proportions of Fe and O are almost equal, and in C the intensity of O is higher than Fe. Point analyses of these areas were taken. The content in area A was 87.2 mol% Fe, in area B was 42.5 mol% Fe and 47.7 mol% O and in area C was 40.7 mol% Fe and 48.8 mol% O. In the image of (a), the white areas of Fe, the dark gray areas of Fe plus O and the light gray areas of C plus S (coal) correspond to reduced iron, wustite (FeO) and carbon, respectively. The black color areas correspond to other elements or empty space. Wustite was not always reduced to iron at the contact with carbon but in several points. This result is in agreement with electron microscope observations reported by Chen *et al.*[4)] They indicated that in the self-reduction process of iron ore concentrates containing coal heated by microwave; magnetite grains were initially reduced around coal grains to form metal iron granular structure.

CONCLUSIONS

Magnetite powder mixed with graphite was heated in nitrogen gas by microwave with 2.45GHz. From the compositions of CO and CO_2 gases in out gas, the reaction rate of the reduction of Fe_3O_4 to Fe through FeO was measured. The reaction process was classified in 3 stages. In the first stage, the temperature was sharply increased and Fe_3O_4 powder was directly reduced to FeO by carbon powder. In the second stage, the temperature of sample was kept at about 600℃ and the reaction almost ceased. After then the temperature again increased and the reduction of FeO to Fe proceeded. In the third stage, the reduction was completely finished and the reduced iron particles absorbed carbon to melt as pig iron.

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