Reduction and Gasification Characteristics of A Unique Iron Ore/carbon Composite Prepared from Robe River and A Coal Tar Vacuum Residue

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We have prepared a unique iron ore/carbon composites (IOC) from a low grade iron ore called Robe River and a thermoplastic carbonaceous material. When Robe River which contains iron as goethite, FeOOH , is heated up to 250 to 300°C, the OH groups are removed as H_2O , leaving flat pore spaces of 0.8 nm wide between 2.0 nm thick Fe_2O_3 layers. The pore spaces are, however, closed over 300°C by the sintering of the Fe_2O_3 layers. The idea proposed is to insert the thermoplastic carbonaceous material into the pore space of 0.8 nm wide while the pore spaces are opened and to carbonize it to form carbon in the pore space below 500°C. The iron oxide in the IOC thus prepared is reduced very rapidly in inert atmosphere and the carbon retained in the pore space is gasified by CO_2 very rapidly also. In this work the reaction characteristics of the unique iron ore/carbon composite prepared from Robe River and a coal tar vacuum residue, CTVR, were examined for its direct reduction, indirect reduction in a H_2 atmosphere, and coke gasification in a CO_2 atmosphere from the viewpoints of reaction enthalpies and rate parameters. The examinations clarified that the carbonaceous material retained as coke in the pore space of iron ore are very reactive and show reaction characteristics different from bulk carbon.

KEY WORDS: iron ore/carbon composite; rapid reduction of iron ore; low grade iron ore; goethite; enthalpy of reduction; rapid gasification of carbon.

1. Introduction

In recent years a raw material forming fine iron ore particles and carbon material as briquette or pellet was proposed as a new feedstock of blast furnace.^{1–5)} We call this new raw material “iron ore/carbon composite (IOC)” in this paper. IOC has been developed with several purposes such as effective utilization of fine iron ore, a coke alternative with high gasification rate of carbon to CO_2 , and enhancement of direct reduction reaction. It is believed that the gasification of carbon in the IOC is enhanced by the catalytic effect of iron ore particles, and the direct reduction is enhanced by the intimate contact of iron ore particles and carbon material in the IOC. The rates of the direct reactions for several IOC samples were examined by Iguchi *et al.*^{6,7)} The reaction rates were, however, rather small below 1 000°C. Kasai *et al.*⁸⁾ examined the reactions involved in the reduction of IOC sample by preparing IOC samples through mixed-grinding of carbonaceous material and iron oxide. They found that the reduction rate was increased with the increase of milling time. They presumed that the increase

was brought about by the catalytic effect and/or change of the rate limiting step from the gasification of carbon to the direct reduction reactions. However, the discussion was all for the reactions around 1 000°C or over. Kashiwaya *et al.* examined the effect of the mixed-grinding on the reduction rate in more detail using hematite-graphite mixture in a series of works.^{9–12)} They have found that the milling in an Ar atmosphere for 1 000 h decreased the reduction reaction peak temperature to as low as 700°C. This dramatic effect was realized by the changes in not only the particle size but in the crystalline sizes of both iron ore and carbon during the milling, enhancing the direct reactions between solid iron oxide and carbon. This is interesting finding, but 1 000 h milling will not be realistic for practical application. The occurrence of the direct reactions at around 700°C was also confirmed by *in-situ* TEM observation between a wuestite and carbon deposited on it.¹³⁾

We have reported that nano-sized Fe_2O_3 particles wrapped by a thermoplastic carbon material are reduced to Fe in several min at as low as 650°C in a N_2 atmosphere, and that the plastic carbon surrounding the Fe_2O_3 particles is gasified completely in several min at as low as 700°C in a CO_2 atmosphere.¹⁴⁾ It was found that the dramatic enhancement of the both reaction rates was realized by the enhancement of the

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direct reduction reaction. To realize this concept practically, we have prepared a unique iron ore/carbon composite (IOC) from a low grade iron ore, Robe River, and thermoplastic carbonaceous material.¹⁵⁾ When Robe River is heated over 250°C, dehydration reaction takes place and slit like pores of 0.8 nm width are formed between the layered Fe_2O_3 of 2.0 nm width.¹⁶⁾ The plastic carbon was inserted into the pores just by heating the mixture of Robe River and the plastic carbonaceous material. When the mixture is heated up to 500°C to prepare IOC, the carbonaceous material is pyrolyzed to produce light oil leaving the heavy fraction as coke within the nano-sized pores.¹⁷⁾ Robe River transformed to Fe_3O_4 in the IOC is reduced to Fe by solid-solid reaction between the layered Fe_3O_4 and the layered coke in several min at less than 900°C. It was also found that the coke in the IOC is gasified very rapidly in both CO_2 and H_2O atmospheres by the catalytic effect of the layered Fe_3O_4 . Thus the proposed IOC is expected to be a new and unique raw material for iron making.

It was judged that both the rapid reduction of iron ore and the rapid gasification of coke are realized by intimate contact of iron ore and coke with large interfacial area. It is well expected that the nano-sized coke retained in the pore space in the IOC will show reaction characteristics different from those of bulk carbon. It is also interesting to investigate how the iron ore in the IOC will be reduced by H_2 .

The purposes of this work are to examine the reaction characteristics of the IOC to direct reduction, indirect reduction in a H_2 atmosphere, and coke gasification in a CO_2 atmosphere from the viewpoints of reaction enthalpies and rate parameters. The IOC sample used for these purposes was prepared from Robe River and a coal tar vacuum residue. To estimate the reaction enthalpies, a TG-DSC analyzer which can simultaneously measure weight change and heat generation rate was used. A methodology to extract the heat generation rate coming from the reactions was developed for this purpose. To obtain the rate parameters, the weight change curves measured at three different heating rates were analyzed by the so called isoconversion method.

2. Experimental

2.1. IOC Sample Used

Tables 1 and 2 respectively show the properties of the iron ore, Robe River (abbreviated to RR), and a coal tar vacuum residue (CTVR) used as the carbonaceous material. Most of Fe in Robe River exists as goethite, judging from

the LOI (ignition loss) value. Robe River ground into less than 150 μm and CTVR powder was mixed at 3 to 1 mass ratio and the mixture was formed to make pellet of 14 mm ϕ and 8 to 10 mm high under the load of 40 MPa. The pellet was heated to 500°C in a nitrogen atmosphere to prepare the iron ore/carbon composite (IOC). The IOC ground into less than 150 μm was served to experiments. Figure 1 shows the XRD profile of the IOC obtained using an X-ray diffractometer (RIGAKU Co. Ltd, Ultima IV). It shows distinct peaks attributed to only Fe_3O_4 , indicating that the carbon inside the IOC, which we call coke in this paper, exists as amorphous carbon. The composition of the IOC by assuming that iron exists solely as Fe_3O_4 is given in Table 3. The carbon to Fe molar ratio (C/Fe) estimated is 2.21 which is larger than the stoichiometric value of the direct reduction reaction given by Reaction (1) given below (= 1.33).

To examine the properties of coke inside the IOC, the IOC was treated by HF to recover the coke by dissolving the Fe_3O_4 . The XRD profile and TEM photos, obtained by a TEM spectrometer (JEOL, JEM-1010), of the coke are respectively shown in Figs. 1 and 2. The TEM photos show that the recovered coke (Dem coke) looks like small thin layered graphene like carbons. Reflecting this structure, the XRD of the Dem coke shows rather broad peaks attributed to graphite. Figure 3 shows the N_2 adsorption/desorption isotherms of the Dem coke, the Robe River heated to 315°C in a nitrogen atmosphere, and the IOC measured using a nitrogen adsorption apparatus (BEL JAPAN Inc., BELSORP-mini.). The Robe River heated to 315°C had as large as 75 m^2/g of BET surface area which comes from the slit shaped pores formed by the dehydration of the Robe River as stated in Introduction. On the other hand, the IOC showed no appreciable N_2 adsorption, which indicates that

Fig. 1. XRD profiles of the samples used. (Online version in color.)

Table 1. Analysis of Robe River.

D_p [μm]	Composition [wt%]						
	Total .Fe	FeO	SiO_2	Al_2O_3	CaO	MgO	LOI*
<150	55.82	0.11	5.85	2.73	0.3	0.23	10.63

Table 2. Analysis of coal tar VR.

Ultimate Analysis [wt%, d.a.f.]				Proximate Analysis [wt%, d.b.]		
C	H	N	S+O (Diff)	VM	FC	Ash
90.7	3.1	1.5	4.8	49.6	51.3	0.05

Table 3. Composition of the IOC used.

	Composition [kg/kg-IOC]				C/Fe [mol/mol]
	Fe_3O_4	As Fe	C	Others	
IOC (500°C)	0.681	0.493	0.235	0.084	2.21

Fig. 2. TEM images of the demineralize coke. (Online version in color.)

Fig. 3. Adsorption/desorption isotherms of the samples used. (Online version in color.)

the entire pore space of the Robe River that is formed by the hydration is occupied by the coke. The coke and the Fe_3O_4 surface are so intimately contacting that nitrogen

cannot penetrate the pores. Very interestingly, however, the N_2 adsorption/desorption isotherm of the Dem coke showed big hysteresis and the BET surface area calculated from the adsorption isotherm was as large as $36 \text{ m}^2/\text{g}$. This shows that the coke is disintegrated when Fe_3O_4 was removed from IOC by the HF treatment and stacking structure of small thin layered graphene like carbons is formed as stated above. The IOC and the Dem coke having such unique properties were used as starting materials in this work.

2.2. Apparatus and Procedure to Estimate Reaction Enthalpies

One of the purposes of this work is to measure the reaction enthalpies of the direct reduction, indirect reduction by H_2 , and the gasification of coke by CO_2 . To do so, we intended to use a TG-DSC analyzer (NETZSCH, STA449 F3) by which we can measure the weight change and the heat generation rate simultaneously using a same sample. When the weight change is related to the degree of reaction, the reaction enthalpy is easily estimated. DSC is very sensitive to detect the sensible heats of sample and sample holder and heat generation/absorption by phase change of sample. Since we want to extract only the heat generation/absorption signal coming from the reaction in focus, we must subtract the signal coming from sensible heats of sample and sample holder from the total signal. In strict sense it is almost impossible to do so, because the amount of sample changes with the progress of reaction and the sensible heat of sample changes accordingly. Then some approximate treatment is necessary to extract the heat generation/absorption signal coming from the reaction in focus. For the TG measurement using the TG-DSC, buoyancy correction is essential for the TG signal.

First, the weight changes of IOC by the three reactions in focus were examined. The overall stoichiometry of the three reactions in focus are respectively represented by

The relative weight of the IOC after completion of the three reactions can be calculated by following the reaction stoichiometry with the aid of the composition given in Table 3 as 0.671 for the direct reduction, 0.812 for the indirect reduction, and 0.765 for the gasification. These calculations indicate that the weight change of the IOC sample is rather small. This suggests that the heat absorption coming from sensible heats of sample and sample holder may be approximately estimated by performing the exactly same measurement using the IOC sample just being reacted to the completion of reaction. The validity of this methodology was examined using the following pyrolysis reaction:

Figure 4 shows the result of simultaneous TG and DSC measurements using a reagent grade CaCO_3 . First, about 14 mg of powdered CaCO_3 was heated in a N_2 stream flow-

Fig. 4. TG-DSC profiles for the thermal decomposition of CaCO_3 . (Online version in color.)

ing at 100 mL/min using the TG-DSC analyzer by following the temperature profile shown by the green solid line. The TG and DSC profiles obtained are respectively shown by the thin dot lines of black and red (1st measurement). The DSC profile showed a large endothermic peak having a maximum at around 800°C in parallel to the sharp decrease of the sample weight, but it deviated from the baseline when the reaction was completed. Next, the remaining CaO was cooled down to room temperature in the TG-DSC analyzer in the N_2 stream, and it was heated again by following the exactly same temperature profile in the N_2 stream to obtain the 2nd TG and DSC profiles, which are respectively shown by the thick broken lines of black and red. The TG profile of the 2nd measurement almost exactly followed that of the 1st measurement up to over 600°C, whereas the DSC signal of the 2nd measurement gradually decreased, which indicates gradual increase of endothermic rate, and finally almost exactly coincided with the DSC signal of the 1st measurement. Then the 2nd TG and DSC signals were subtracted from the corresponding 1st signals to obtain corrected signals shown respectively by the thick solid lines of black and red (2nd – 1st). The corrected TG signal showed smooth and rapid weight decrease over 600°C and the completion of the reaction at around 800°C. The final weight was almost exactly same as the weight expected from the reaction stoichiometry, indicating that the buoyancy correction could be done successfully. The corrected DSC signal showed large endothermic peak in parallel to the weight decrease and returned to the baseline at the completion of reaction, suggesting the validity of the methodology. The corrected DSC signal was integrated against time to obtain the accumulated amount of heat generated, which was then plotted against the weight decrease as shown in Fig. 5. The slope at a specified point gives the local value of the reaction enthalpy in the unit of kJ/kg. Since the weight change is plotted to the direction of weight decrease, namely to the direction of reaction progress, the downward-sloping curve shows endothermic reaction. The slopes corresponding to the thermodynamic reaction enthalpies at three temperatures of 700, 750, and 800°C are shown by red broken lines. The slopes of the measured relationship between the accumulated amount of heat and the weight decrease were so close to those of the broken lines. These examinations showed the validity of the proposed methodology to extract the DSC signal coming solely from reaction.

Fig. 5. Relationship between the accumulated amount of heat generated and weight change for the thermal decomposition of CaCO_3 . (Online version in color.)

Based on the preliminary experiment, the 1st experiments to obtain the reaction enthalpies of the three reactions in focus were performed as follows:

- Direct reduction of Fe_3O_4 in the IOC: 15 to 30 mg of the IOC sample was heated from 500°C at the rate of 5, 10, or 20 K/min in a N_2 stream flowing at 100 mL/min using the TG-DSC analyzer. The product gas formed after 500°C was analyzed for CO , CO_2 , and H_2O in every one minute using a micro gas chromatograph (GL Science, Micro GC CP 4900).
- Indirect reduction of Fe_3O_4 in the IOC by H_2 : 15 to 30 mg of the IOC sample was heated at the rate of 5, 10, or 20 K/min up to 900°C in a mixed gas stream of 10% H_2 and 90% N_2 ($\text{H}_2(10\%)/\text{N}_2$) flowing at 100 mL/min using the TG-DSC analyzer. For comparison purpose, an experiment using Robe River itself was also performed.
- Gasification of coke by CO_2 : About 30 mg of the IOC sample was heated at the rate of 10 K/min up to 1 000°C in a gas stream of CO_2 flowing at 100 mL/min using the TG-DSC analyzer.

For all the TG-DSC measurements, 2nd experiments were performed as were done for the pyrolysis of CaCO_3 , and the signals subtracting 2nd signals from 1st signals were used for estimating the reaction enthalpies. The effects of gas streams on the magnitude of DSC signals were also corrected. The relative sensitivities to the N_2 stream were determined to be 1.15 for CO_2 stream and 2.77 for the mixed gas stream of 10% H_2 and 90% N_2 from preliminary experiments.

2.3. Apparatus and Procedure to Estimate Rate Parameters

For (a) direct reduction and (b) indirect reduction by H_2 , the TG curves obtained using the TG-DSC analyzer at the heating rate of 5, 10, or 20 K/min were used. For (c) coke gasification, about 30 mg of the IOC sample was heated at the rate of 5, 10, or 20 K/min up to 1 100°C in a gas stream of CO_2 flowing at 100 mL/min using a TG analyzer (Shimadzu, TG-50H). The TG curves were analyzed by the so called isoconversion method to obtain local activation energies. Several reaction models were tested to formulate the rate equations as described in detail below.

3. Results and Discussion

3.1. TG and DSC Signals Obtained by the Proposed Methodology

Figures 6 to 8 respectively show the TG-DSC profiles measured at the heating rate of 10 K/min for (a) direct reduction, (b) indirect reduction by H_2 , and (c) coke gasification. For all the measurements, the TG signals of 1st–2nd show smooth changes and the DSC signals returned to the baseline when the reactions were completed, suggesting the validity of the proposed methodology to get reliable

Fig. 6. TG-DSC profiles for the direct reaction experiment of IOC. (Online version in color.)

Fig. 7. TG-DSC profiles for the indirect reaction experiment of IOC in $H_2(10\%) / N_2$ atmosphere. (Online version in color.)

Fig. 8. TG-DSC profiles for the coke gasification experiment CO_2 atmosphere. (Online version in color.)

TG and DSC signals. Figure 9 shows the TG-DSC profiles measured at the heating rate of 10 K/min for the indirect reduction of Robe River itself by H_2 . Again the TG signal of 1st – 2nd showed smooth changes and the DSC signal returned to the baseline when the reaction was completed.

3.2. Weight Change and Degree of Reaction

It is essential to know how the weight change is related to the degree of reaction to estimate the reaction enthalpy from the heat generation and the weight change. Then the normalized weight changes, W/W_0 , and the heat generation rates per unit weight of sample, dQ/dt , calculated from Figs. 6 to 9 are shown against temperature in Fig. 10. Figure 11 shows the XRD profiles of the solid products remaining after the TG-DSC measurements with the XRD profile of the IOC. The iron species detected were Fe and Fe_3C after the direct reduction experiment and only Fe for the IOC and Robe River after the indirect reduction experiments in the $H_2(10\%) / N_2$ stream. The XRD spectrum for the IOC after the coke gasification experiment was almost same as that of the unreacted IOC and showed peaks coming from only Fe_3O_4 . The final relative weight of the IOC after the indirect reduction experiment was 0.72 which was smaller than the value of 0.812 estimated by following the reaction stoichiometry of Reaction (2). On the other hand, the final relative weight of the Robe River after the indirect reduction experiment was 0.73 which was exactly equal to the value of 0.731 estimated by assuming that iron in Robe River exists solely as Fe_2O_3 at 300°C and Fe_2O_3 was completely reduced to iron. The final relative weight of the IOC after the coke gasification experiment was 0.76 which was almost equal to the value of 0.765 estimated by following the reaction stoichiometry of Reaction (3). These examinations show that the weight changes are proportional to the expected reaction degrees for the indirect reduction of Robe River and the gasification of coke in the IOC. The larger weight decrease than the expected reaction stoichiometry for the indirect reduction experiment indicates that the reaction of carbon in the IOC with H_2 to produce hydrocarbon gases may occur at low temperature region, although the gas analysis could not detect distinct formation of hydrocarbon gases.

The relationship between the weight change and the degree of reaction was examined with the aid of gas formation behavior for the direct reduction experiment. Figure

Fig. 9. TG-DSC profiles for the indirect reaction experiment of Robe River in $H_2(10\%) / N_2$ atmosphere. (Online version in color.)

Fig. 10. Comparison of weight change and heat generation behaviors among the direct reduction, indirect reduction, and coke gasification of IOC and the direct reduction of Robe River. (Online version in color.)

Fig. 11. XRD profiles of the IOC sample after the direct reduction, indirect reduction, and coke gasification and Robe River after the direct reduction. (Online version in color.)

Fig. 12. TG-DSC profiles for the direct reaction experiment of IOC. (Online version in color.)

12 shows the accumulated amounts of gases formed against temperature for the direct reduction shown in Fig. 6. The reaction degree of the direct reduction was examined using Figs. 11 and 12. The measured weight change (solid line) showed good agreement with the weight change calculated

Fig. 13. Relationship between the accumulated amount of heat generated and weight change during the direct reduction and coke gasification of the IOC sample. (Online version in color.)

from the amount of three gases, CO, CO₂, and H₂O, formed (broken line), indicating that the measured weight change well represents the progress of the reduction. The amount of O existing as Fe₃O₄ in the IOC is calculated to be 0.188 kg/kg from Table 3, whereas the amount of O evolved as CO and CO₂ by 1 100°C is 0.179 kg/kg, and the amount of O evolved as CO, CO₂, and H₂O by 1 100°C is 0.198 kg/kg. Assuming that the reduction of Fe₃O₄ in the IOC was completed by Reaction (1) and the indirect reduction, Reaction (5), by the CO produced by Reaction (1), the overall contributing ratio of the direct reduction, Reaction (1), to the reduction of Fe₃O₄ is calculated to be 0.85 (= (270 + 58) × 10⁻⁶ mol / ((270 + 58 + 58) × 10⁻⁶ mol)).

These results indicates that Fe₃O₄ in the IOC was mostly reduced by the direct reduction reaction, and hence the weight decrease is approximately related to the degree of the direct reduction reaction.

3.3. Estimation of Reaction Enthalpies from the TG-DSC Measurements

The heat generation rates, dQ/dt , shown in Fig. 10 are integrated against time to obtain the accumulated amounts of heat generated, Q . **Figure 13** plots Q against W/W_0 for the direct reduction and the coke gasification as was done for the decomposition of CaCO₃ in Fig. 5. **Figure 14** shows corresponding plots for the indirect reduction of the IOC and Robe River. For every plot, the slope at a specified point gives the local value of the reaction enthalpy in the unit of kJ/kg. Since the weight change is plotted to the direction of weight decrease, namely to the direction of reaction progress, the downward-sloping curve shows endothermic reaction as stated above. The reduction experiments in N₂ is judged to involve the following four reactions:

Fig. 14. Relationship between the accumulated amount of heat generated and weight change for the IOC sample and Robe River during the indirect reduction experiments. (Online version in color.)

The indirect reduction of the IOC by H_2 involves the following reactions:

Tables 4 to 10 show the thermodynamic reaction enthalpies of Reactions (6) to (11) and (3); ΔH_R in the unit of $\text{kJ}\cdot\text{mol}^{-1}$ and Δh_R in the unit of kJ per kg of change of the IOC. The Δh_R values can be compared with the slopes in Figs. 13 and 14.

For the direct reduction experiments, the slopes of the Q vs W/W_0 relationship were respectively 4 950, 2 720, and 2 220 kJ/kg at 650, 800, and 900°C, whereas the Δh_R value of Reaction (6) was 6 810 kJ/kg at 650°C and the Δh_R values of Reaction (7) were respectively 5 360 and 5 400 kJ/kg at 800 and 900°C. The weight change in Fig. 12 shows that the reduction of Fe_3O_4 is occurring at 650°C but the dominant gaseous product is CO_2 . This means that CO formed by Reaction (6) is almost totally consumed by Reaction (8), which gives apparent Δh_R value of 4 770 kJ/kg ($= 0.028 \times 6\,810 \text{ kJ/kg} / (0.028 + 0.016) + 0.016 \times 1\,200 \text{ kJ/kg} / (0.028 + 0.016)$). The value is rather close to the slope value of 4 950 kJ/kg, indicating that the reaction enthalpy is well estimated. On the other hand, it is judged that Reaction (7) producing CO is prevailing at 800 to 900°C, where the slope values are clearly much smaller than the Δh_R values of Reaction (7). The slope values are much smaller than the Δh_R values even if they are calculated by taking into account the contribution of Reaction (8). This shows that the measured reaction enthalpy for the direct reduction of the IOC over 700°C is less than half of the Δh_R value of Reaction (7).

For the coke gasification experiments, the slopes of the Q vs W/W_0 relationship were respectively 3 840, 5 720, and 6 220 kJ/kg at 800, 900, and 950°C, whereas the Δh_R values of Reaction (3) were respectively 14 190, 14 110, and 14 070 kJ/kg at 800, 900 and 950°C. Since just Reaction (3) is judged to occur in the CO_2 atmosphere from Figs. 10 and 11, the measured reaction enthalpies for the gasification of coke by CO_2 are less than half of the thermodynamic reac-

Table 4. Reaction enthalpies of Reaction (6): $\text{Fe}_3\text{O}_4 + \text{C} \rightarrow 3\text{FeO} + \text{CO}$.

T_C [°C]	25	500	550	600	650	700	800
ΔH_R [$\text{kJ}\cdot\text{mol}^{-1}$]	214	204	200	196	191	185	173
Δh_R [$\text{kJ}\cdot\text{kg}\cdot\text{CO}^{-1}$]	7 650	7 280	7 140	6 980	6 810	6 620	6 180

Table 5. Reaction enthalpies of Reaction (7): $\text{FeO} + \text{C} \rightarrow \text{Fe} + \text{CO}$.

T_C [°C]	25	600	700	800	900	1 000
ΔH_R [$\text{kJ}\cdot\text{mol}^{-1}$]	154	149	150	150	151	153
Δh_R [$\text{kJ}\cdot\text{kg}\cdot\text{CO}^{-1}$]	5 490	5 340	5 340	5 360	5 400	5 450

Table 6. Reaction enthalpies of Reaction (8): $\text{Fe}_3\text{O}_4 + \text{CO} \rightarrow 3\text{FeO} + \text{CO}_2$.

T_C [°C]	25	500	550	600	650	700	800
ΔH_R [$\text{kJ}\cdot\text{mol}^{-1}$]	41.8	31.2	27.7	23.7	19.20	14.22	2.77
Δh_R [$\text{kJ}\cdot\text{kg}\cdot\text{O}^{-1}$]	2 610	1 950	1 730	1 480	1 200	889	173.4

Table 7. Reaction enthalpies of Reaction (9): $\text{FeO} + \text{CO} \rightarrow \text{Fe} + \text{CO}_2$.

T_C [°C]	25	600	700	800	900	1 000
ΔH_R [$\text{kJ}\cdot\text{mol}^{-1}$]	-18.58	-22.4	-21.4	-20.0	-18.18	-15.82
Δh_R [$\text{kJ}\cdot\text{kg}\cdot\text{O}^{-1}$]	-1 162	-1 398	-1 340	-1 253	-1 136	-989

Table 8. Reaction enthalpies of Reaction (10): $\text{Fe}_3\text{O}_4 + \text{H}_2 \rightarrow 3\text{FeO} + \text{H}_2\text{O}$.

T_C [°C]	25	400	450	500	550	600
ΔH_R [$\text{kJ}\cdot\text{mol}^{-1}$]	83.0	74.8	71.7	68.2	64.1	59.6
Δh_R [$\text{kJ}\cdot\text{kg}\cdot\text{O}^{-1}$]	5 190	4 670	4 480	4 260	4 010	3 730

Table 9. Reaction enthalpies of Reaction (11): $\text{FeO} + \text{H}_2 \rightarrow \text{Fe} + \text{H}_2\text{O}$.

T_C [°C]	25	500	550	600	650	700	750
ΔH_R [$\text{kJ}\cdot\text{mol}^{-1}$]	22.6	14.2	13.8	13.6	13.4	13.5	13.6
Δh_R [$\text{kJ}\cdot\text{kg}\cdot\text{O}^{-1}$]	1 410	885	862	848	841	841	850

Table 10. Reaction enthalpies of Reaction (3): $\text{C} + \text{CO}_2 \rightarrow 2\text{CO}$.

T_C [°C]	25	600	700	800	900	1 000
ΔH_R [$\text{kJ}\cdot\text{mol}^{-1}$]	172	172	171	170	169	168
Δh_R [$\text{kJ}\cdot\text{kg}\cdot\text{C}^{-1}$]	14 370	14 320	14 260	14 190	14 110	14 030

tion enthalpies.

For the indirect reduction experiments, the slopes of the Q vs W/W_0 relationship for the Robe River were respectively 4 640 and 860 kJ/kg at 400 and 600°C, whereas the Δh_R value of Reaction (10) is 4 670 kJ/kg at 400°C and the Δh_R value of Reaction (11) is 848 kJ/kg at 600°C. On the

other hand, the slope of the Q vs W/W_0 relationship for the IOC was almost constant over 650°C and was, for example, 810 kJ/kg at 700°C. Since it was expected that Reaction (11) is dominant at higher temperature region, the slope value is expected to correspond to the Δh_R value of Reaction (11). Actually the Δh_R value of Reaction (11) is 841 kJ/kg at 700°C as given in Table 9. At lower temperature region the hydrogenation reaction of carbon in the IOC to produce hydrocarbon gas, which is exothermic reaction, is judged to occur. Then the slopes at lower temperature region come from Reaction (10) and the hydrogenation reaction, resulting in rather small slopes.

Summarizing the above discussion, the measured reaction enthalpies for the indirect reduction were rather close to those of thermodynamic reaction enthalpies when dominant reactions are identified, indicating not only the validity of the proposed methodology to estimate the reaction enthalpies but the little effect of the peculiar IOC structure to the indirect reduction reaction. On the other hand, the measured reaction enthalpies of both the direct reduction and the coke gasification were much smaller than the corresponding thermodynamic reaction enthalpies. This may come from the uniqueness of coke and intimate contact between the coke and the iron oxides. Some intermediate products which are different from bulk carbon and/or iron oxides may have been formed in the IOC.

3.4. Determination of Activation Energies of the Three Reactions from TG Measurements

The changing rate of conversion of solid reactant, dX/dt , is usually represented by the following equation for heterogeneous reactions such as pyrolysis, gas-solid reaction, etc.

$$\frac{dX}{dt} = k_0 e^{-E/RT} f(X) \quad (12)$$

where t is the time, k_0 is the apparent frequency factor, E is the activation energy, T is the temperature, R is the gas constant, and $f(X)$ represents some function of only solid conversion X . The apparent frequency factor k_0 is constant for pyrolysis but it is some function of the pressures of gaseous reactants for gas-solid reaction. However, it can be regarded as a constant when the pressures of gaseous reactants are kept constant as were for (b) indirect reduction and (c) coke gasification experiments of this work. For (a) direct reduction, both iron oxide and carbon are solid reactants, but the conversion of carbon is related to the conversion of iron ore. Then Eq. (12) is valid for (a) direct reduction also.

In this work the so called temperature programmed reaction technique that heats up solid samples from a low temperature T_0 under a constant heating rate a was used to examine the three reactions, where weight change versus temperature relationships are utilized to extract the rate parameters of the reactions. The temperature of solid sample T is related to time t by

$$T = T_0 + at \quad (13)$$

Inserting Eq. (13) into Eq. (12) gives

$$\frac{dX}{dT} = \frac{k_0}{a} e^{-E/RT} f(X) \quad (14)$$

This equation can be formally integrated to give X versus T relationship as

$$g(X) = \int_0^X \frac{dX}{f(X)} = \frac{k_0}{a} \int_{T_0}^T e^{-E/RT} dT \cong \frac{k_0}{a} \int_0^T e^{-E/RT} dT \quad (15)$$

It is stressed here that integration is performed under the conditions of constant k_0 and E . Using the approximation proposed by Doyle,¹⁸⁾ Eq. (15) is represented as

$$g(X) = \frac{k_0}{a} \int_0^T e^{-E/RT} dT = \frac{k_0 E}{aR} \left(\frac{e^{-u}}{u} - \int_u^\infty \frac{e^{-u}}{u} du \right) \quad (16)$$

$$= \frac{k_0 E}{aR} p(u) \cong k_0 e^{-E/RT} \times \frac{RT^2}{aE}$$

where $p(u)$ is set equal to e^{-u}/u^2 . This approximation is known to be very accurate for $u = E/RT > 15$.

When the form of $f(X)$ is unknown, a method which is called isoconversion method can be employed. Taking the logarithm of both sides, Eq. (16) can be rearranged to give

$$\ln \left(\frac{a}{T^2} \right) = \ln \left(\frac{k_0 R}{E} \right) - \ln g(X) - \frac{E}{RT} \quad (17)$$

Since $g(X)$ is same at a selected X value for different heating rates, the Arrhenius plots of $\ln(a/T^2)$ vs. $1/T$ gives E value at the conversion X . It should be stressed here that the Arrhenius plots at different X levels should be in parallel if the reaction system consists of single reaction. If the Arrhenius plots are not in parallel, the reaction system cannot be represented by single reaction. This means that the analysis using Eq. (17) must be discarded, because Eq. (17) was obtained by integrating Eq. (14) by assuming constant k_0 and E values. This analysis method is often called the Kissinger-Akahira-Sunose method.¹⁹⁾

Overcoming the weakness of the analysis method, Miura and Maki have shown that the Arrhenius plots of $\ln(a/T^2)$ vs. $1/T$ gives local activation energies for multiple reactions also.²⁰⁾ If the reaction in focus consists of N parallel reactions, the changing rate of the conversion of the i -th reaction, dX_i/dt , can be written in analogy to Eq. (12) as

$$\frac{dX_i}{dt} = k_{0i} e^{-E_i/RT} f_i(X_i) \quad (18)$$

where the subscript i means the i -th reaction and the overall conversion X is given by $X = \sum_{i=1}^N X_i$ using the fractional contribution of every reaction X_{i0} defined by $\sum_{i=1}^N X_{i0} = 1$. Equation (18) can be integrated to give

$$g_i(X_i) \cong k_{0i} e^{-E_i/RT} \times \frac{RT^2}{aE_i} \quad (19)$$

Taking logarithm of both sides, Eq. (19) can be rearranged to give

$$\ln \left(\frac{a}{T^2} \right) \cong \ln \left(\frac{k_{0i} R}{E_i} \right) - \ln g_i(X_i) - \frac{E_i}{RT} \quad (20)$$

Since it is a good approximation to assume that only the i -th reaction is taking place at a certain conversion X , the Arrhenius plots of $\ln(a/T^2)$ vs. $1/T$ at the conversion X gives

the activation energy of the i -th reaction, E_i .

The above discussion shows that the W/W_0 vs. T relationships measured at 3 different heating rates are enough to estimate E values covering whole reaction range. **Figure 15** shows the W/W_0 vs. T relationships for (a) direct

Fig. 15. Relationship between the relative weight, W/W_0 , and temperature measured at three different heating rates for the direct reduction experiments of the IOC. (Online version in color.)

Fig. 16. The Arrhenius plots of $\ln(a/T^2)$ vs. $1/T$ at same W/W_0 levels for the direct reduction experiments of the IOC. (Online version in color.)

Fig. 17. Activation energies estimated for the three reaction systems. (Online version in color.)

reduction as an example. The Arrhenius plots of $\ln(a/T^2)$ performed at several same W/W_0 levels are typically shown for (a) direct reduction in **Fig. 16**. By performing similar plots for both (b) indirect reduction and (c) coke gasification, changes of activation energies with temperature at $a = 10$ K/min and W/W_0 are shown in **Fig. 17** for the three reactions. It was judged that every reaction involves at least two reactions and every activation energy was estimated to be as follows:

(a) Direct reduction: $E_1 \cong 310$ kJ/mol, $E_2 \cong 230 - 240$ kJ/mol

(b) Indirect reduction: $E_1 \cong 90$ kJ/mol, $E_2 \cong 200$ kJ/mol

(c) Coke gasification: $E_1 \cong 215$ kJ/mol, $E_2 \cong 310$ kJ/mol

Judging from the range of W/W_0 values, the first and second reactions of (a) direct reduction are assumed to be respectively for Reaction (6) and Reaction (7), and the first and second reactions of (b) indirect reduction are assumed to be respectively for Reaction (10) and Reaction (11). Although it is very strange that E_1 is larger than E_2 for (a) direct reduction, we cannot explain the reason at the present. It is also interesting to note that two reactions are involved for (c) coke gasification. This may suggest that there exists two types of coke in the IOC. The rapid gasification of coke was judged to proceed by the redox cycle of Fe_3O_4 as shown by Reactions (6) and (21).¹⁵ The sum of these two reactions forms the gasification reaction (3). Since Reaction (6) is controlling the rate of gasification of coke, the activation energy of coke gasification should coincide with that of the direct reduction reaction (6). The activation energy of Reaction (6) is $\cong 310$ kJ/mol as discussed above, and the 2nd activation energy of coke gasification is also $\cong 310$ kJ/mol. This agreement suggests the soundness of the activation energies estimated.

As far as the authors know, little works have been performed to estimate the activation energies of both (a) direct reaction and (b) indirect reduction. Takahashi *et al.*²¹⁾ reported in 1971 that the overall activation energy of the reduction of an iron oxide pellet by H_2 was 26 kcal/mol (= 109 kJ/mol) in the temperature range of 1 100 to 1 400 K. Although it may not be directly compared with the activation energies of this work, it is rather close to E_1 value of (b) in direct reduction.

3.5. Formulation of Rate Equation for Coke Gasification

Next, it was intended to estimate the fractional contributions X_{10} and X_{20} and to formulate the functions $f_1(X_1)$ and $f_2(X_2)$ for every reaction system. To do so, several reaction models given in **Table 11** were tested. Models (a) to (c) are often used for the analysis of gas solid reactions,²²⁾ and (d) Avrami model is well known to represent the change of X flexibly and is applied to analyze nucleation reaction.²³⁾ The values of X_{i0} and $f_i(X_i)$ can be estimated by the following procedure.

As stated above, Eq. (16) gives the relationship between X and $k_0\tau_a$ ($=k_0e^{-E/RT} \frac{RT^2}{aE}$) through $g(X)$ given in Table 11. Then the X vs $k_0\tau_a$ diagrams, which we call mother diagrams, were constructed for all of the reaction models by taking $k_0\tau_a$ axis logarithm scale as shown in Figs. 18(a) and 18(b). Then the following procedure is applied for single reactions with known E values.

- ① Plot X against $\tau_a (=e^{-E/RT}(RT^2/aE))$ taking the τ_a axis logarithm scale on the same size of section paper at all the heating rates of three or more. The plots will coincide each other if the activation energy was correctly estimated. Let us call the plot $X-\tau_a$ diagram.
- ② Superimpose the mother diagrams on the $X-\tau_a$ diagram to find a most suitable X vs. $k_0e^{-E/RT}(RT^2/aE)$ relationship that fits the $X-\tau_a$ diagram. The functional form $f(X)$ can be estimated from the superimposition.
- ③ Comparing the abscissas of the mother diagram and the $X-\tau_a$ diagram at the best superimposition, k_0 can be obtained.

For multiple reactions, the above procedure is applied for individual reactions constituting the multiple reactions. For (c) coke gasification, it was judged that the first reaction covers $0.68 < 1-X < 0.9$ and the second stage covers $0 < 1-X < 0.68$ by iterative trials. This means that $X_{10} = 0.32$ and $X_{20} = 0.68$. Then new conversions X_1 and X_2 can be calculated using the $1-X$ vs T relationships and the X_{10} and X_{20} estimated. X_1 and X_2 were respectively plotted

against $\tau_{a1} (=e^{-E_1/RT}(RT^2/aE_1))$ with $E_1 = 215$ kJ/mol and $\tau_{a2} (=e^{-E_2/RT}(RT^2/aE_2))$ with $E_2 = 309$ kJ/mol. Then the above procedure was applied for the two reactions to estimate $f_1(X_1)$, k_{01} , $f_2(X_2)$, and k_{02} . Finally the rate equations for the two reactions were estimated as follows:

1st reaction:

$$\frac{dX_1}{dt} = k_{01}e^{-E_1/RT}(1-X_1)^{3/2} \text{ with } E_1 = 215 \text{ kJ/mol, } k_{01} = 1.94 \times 10^8 \text{ s}^{-1} \dots\dots\dots (22)$$

2nd reaction:

$$\frac{dX_2}{dt} = k_{02}e^{-E_2/RT}(1-X_2) \text{ with } E_2 = 309 \text{ kJ/mol, } k_{02} = 7.14 \times 10^{10} \text{ s}^{-1} \dots\dots\dots (23)$$

Equations (22) and (23) are integrated to give respectively Eqs. (24) and (25).

$$1-X_1 \cong 4 \sqrt{\left(2 + k_{01}e^{-E_1/RT} \cdot \frac{RT^2}{aE_1}\right)^2} \dots\dots\dots (24)$$

$$1-X_2 \cong \exp\left(-k_{02}e^{-E_2/RT} \cdot \frac{RT^2}{aE_2}\right) \dots\dots\dots (25)$$

Figure 19 compares the experimentally obtained $1-X$ vs T relationships and the calculated ones using Eqs. (24) and (25). Good agreements between the experimental and calculated $1-X$ vs T relationships for all heating rates suggest the validity of the rate equations obtained. The first reaction, however, was strangely represented by a 3/2-th order reaction which is rarely encountered in gas solid reactions. To analyze the first reaction, the mother curves for several n -th order reactions were constructed as shown by the red curves in Fig. 18(a). The activation energy of the 1st reaction, E_1 , was also much smaller than those reported on the C-CO₂ reaction. These results for the rate parameters with low reaction enthalpies obtained for the direct reduction and coke gasification suggests the uniqueness of coke in the IOC.

It was also intended to formulate rate equations for both

Table 11. $f(x_B)$ and $g(x_B)$ for several reaction models.

Reaction model	$f(X)$	$g(X)$
(a) Volume reaction model (VR Model)	$1-X$	$-\ln(1-X)$
(b) Simple grain model (Grain Model-1)	$(1-X)^{2/3}$	$3\{1-(1-X)^{1/3}\}$
(c) Random Pore Model (RP Model)	$(1-X)\sqrt{1-\psi\ln(1-X)}$	$\frac{2}{\psi}\{\sqrt{1-\psi\ln(1-X)}-1\}$
(d) Avrami Erofe'ev (Avrami Model)	$\alpha(1-X)[-\ln(1-X)]^{(\alpha-1)/\alpha}$	$[-\ln(1-X)]^{1/\alpha}$

Fig. 18. Mother diagrams showing the relationships between X and $k_0\tau_a$ ($=k_0e^{-E/RT} \frac{RT^2}{aE}$). (Online version in color.)

Fig. 19. Comparison between the experimentally obtained $1-X$ vs T relationships and the calculated ones using Eqs. (24) and (25) for the coke gasification. (Online version in color.)

direct reduction and indirect reduction, but any models in Table 11 fitted the experimental data for the direct reduction. The experimentally obtained X vs. T relationships are too steep to fit the X vs. T relationships of the models due to large reduction rate. For the indirect reduction, it was difficult to find the dominant reaction at low temperature regions, which made it difficult to fit the experimental data to the models tested.

4. Conclusion

The reaction characteristics of a unique iron ore/carbon composite, IOC, prepared from Rove River and a coal tar vacuum residue, CTVR, were examined for its direct reduction, indirect reduction in a H_2 atmosphere, and coke gasification in a CO_2 atmosphere from the viewpoints of reaction enthalpies and rate parameters.

First, a methodology to estimate the reaction enthalpies using a TG-DSC analyzer was proposed using the decomposition of $CaCO_3$ as a model reaction. For both the direct reduction and the coke gasification, the measured enthalpies were found to be less than half of the corresponding thermodynamic reaction enthalpies. For the indirect reduction, on the other hand, the measured reaction enthalpies at higher temperature region were almost same as those of the corresponding thermodynamic reaction enthalpies. For the indirect reduction of Robe River itself which was performed for comparison purpose, the measured reaction enthalpies

over $400^\circ C$ were almost exactly same as those of the corresponding thermodynamic reaction enthalpies.

The activation energies of the reactions were successfully estimated by Miura-Maki method. It was judged that every reaction involves at least two reactions and every activation energy was estimated to be as follows: direct reduction: $E_1 \cong 310$ kJ/mol and $E_2 \cong 230 - 240$ kJ/mol, indirect reduction: $E_1 \cong 90$ kJ/mol and $E_2 \cong 200$ kJ/mol, and coke gasification: $E_1 \cong 215$ kJ/mol and $E_2 \cong 310$ kJ/mol. The rate equations were formulated for the two reactions involved in the coke gasification. The rapid 1st reaction was strangely represented by a 3/2-th order reaction against unreacted coke.

The examinations clarified that the coke retained intimately in the pore space of Fe_2O_3 are very reactive and show reaction characteristics different from bulk carbon.

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