Effect of Mixed-grinding on Reduction Process of Carbonaceous Material and Iron Oxide Composite

Eiki KASAI, Katsuhito MAE[1] and Fumio SAITO

Institute for Advanced Materials Processing, Tohoku University, Katahira, Aoba-ku, Sendai, Miyagi-ken, 980-77 Japan. E-mail: kasai@iamp.ac.jp   1) Formerly Institute for Advanced Materials Processing, Tohoku University. Now at Mie Works, Shokozan Mining, Co. Ltd.

Mixing state and structure of composite significantly influence reduction kinetics of carbonaceous materials/iron oxides mixture. The present study reports the effect of mixed-grinding of the mixture on the reduction of the composite by indirect heating. Mixtures prepared by different combinations of hematite and graphite reagents, iron ores and metallurgical coke were mixed-ground by two types of ball mills. TG-DTA measurements for the composites were carried out under different heating patterns and total pressures. Reaction temperature remarkably decreases by the mixed-grinding operation in any combinations of materials and total pressures. A catalytic effect of iron produced during reaction is observed when using graphite reagents but seems to be inhibited when using metallurgical coke. A simple kinetic analysis suggests that gasification of carbon is promoted through enhancement of the catalytic effect and/or change of rate limiting step from the gasification of carbon to the direct reactions between iron oxides and carbon.

KEY WORDS: iron ore; coke; graphite; carbon gasification; reduction; mixed-grinding; ball mill; catalytic effect.

1. Introduction

A number of researches[1–14] have been reported on the reaction process of carbonaceous materials/iron oxides composites by indirect heating. These were focused on not only industrial significance for developing new ironmaking processes without using iron ore agglomeration and cokemaking processes but also scientific interests for remarkably complex reactions and phenomena occurring in the process.

The reaction sequence of the process can be represented by

$$Fe_xO_y(g) + CO(g) \rightarrow Fe_xO_{y-1}(s) + CO_2(g) \quad ....(1)$$

$$CO_2(g) + C(s) \rightarrow 2CO(g) \quad ....(2)$$
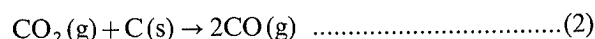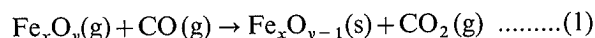
These equations show that the system is not actual solid–solid reactions (Eq. (3)) but the individual gas/solid reactions proceed with gaseous intermediates, CO and CO_2. Further, it is widely accepted[7] that the overall reaction rate is controlled by the solution loss reaction, Eq. (2), at below about 1 100°C.

$$Fe_xO_y(g) + C(s) \rightarrow Fe_xO_{y-1}(s) + CO(g) \quad ....(3)$$
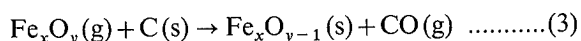
Several studies[5,7,14] have been focused on the effect of particle size of carbonaceous materials. They reported that a decrease in the size leads to a higher reaction rate. However, Ree and Tate[3] have stated that decrease in the particle size of iron oxides increases the reaction rate

more than that of carbonaceous materials. Reactions of Eq. (3), combination of Eqs. (1) and (2), are often called as direct reductions. Although Eq. (3) is stoichiometically meaningful, they are generally regarded as substantially non-operative reactions because they occur at carbon–iron oxide contact points only.[12] However, their significant contribution has been found in the reaction using noncoking coal at high temperatures over 1 000°C.[11] In addition, there are still some arguments such as reduction manner, e.g., stagewise or not, and catalytic effect of metallic iron produced during reduction.

Most of the previous studies have employed a sequential way for the preparation of raw materials, i.e., mixing of carbonaceous materials and iron oxides after their individual crushing/grinding. Crushing/grinding of plural materials, called as mixed-grinding, is a technique to achieve particle size reduction and mixing simultaneously. This has been widely applied in the pretreatment of raw materials of ceramics to improve sintering behavior and formation of finely controlled crystalline textures. Mixed-grinding also induces the formation of composites. For example, a harder particle tends to be wrapped by the layer of softer fine particles. This will enlarge the contact area of materials and thereby promoting solid/solid reactions.

This study aims to clarify the effect of mixed-grinding on the reactions between carbonaceous materials and iron oxides by indirect heating. A conventional tumbling ball mill and a planetary ball mill which is classified as

an intensive grinder are used for grinding of samples. The reaction rate was measured by a thermogravimetry, TG, and differential thermal analysis, DTA, at a constant heating rate and at fixed temperatures after rapid heating.

2. Experimental

2.1. Sample

Hematite reagent, hematite ore A from Brazil and pisolitic ore B from Australia were used as iron oxide samples. Graphite reagent and metallurgical coke are used as carbonaceous materials. Both reagents are originally fine powder state and their specific surface area, SSA, are $11.3 \, \text{m}^2/\text{g}$ for hematite and $8.79 \, \text{m}^2/\text{g}$ for graphite. Chemical and elemental compositions of the other samples are listed in **Tables 1** and **2**. The ore and coke samples were preliminary crushed and sieved into a size range between 125 and 250 μm.

2.2. Pre-mixing

The carbonaceous material and iron oxide samples were preliminary mixed under a wet condition using a unique tumbling ball mill before subjecting it to mixed-grinding. Nylon and polyethylene were employed as materials of ball and pot, respectively, so as to prevent the breakdown of the particles during mixing.

The sample 80 g, ethylalcohol 150 cm³ and fifty nylon balls of 10 mm diameter were put in a polyethylene pot of 500 cm³ inner volume. Then, the pot was rotated at 100 rpm for 2 h. The obtained slurry was dried carefully on a hot magnetic stirrer. By comparison of SSA of samples before and after the mixing, it was confirmed that the particle size reduction of the samples were negligibly small.

2.3. Mixed-grinding

Mixed-grinding of the pre-mixed samples was conducted by using planetary and tumbling ball mills. These mills are hereinafter called as PM and TM, respectively.

For the grinding by PM, 5 g of the sample were charged with seven agate balls of 15 mm diameter into an agate pot of 50 cm³ inner volume. Two pots were placed in the PM and its rotational speed was set at 1 350 rpm. Total grinding time was varied from 5 to 60 min and the

grinding was interrupted for 30 min after every 15 min in order to prevent the temperature of samples from increasing excessively.

In the case of the grinding by TM, the sample 300 g and alumina balls of 20 mm diameter were charged into an alumina pot of 1 000 cm³ inner volume. The occupancy ratio of the balls to the total inner volume of the pot was about 50%. The rotational speed was set at 95 rpm and maximum grinding time was 100 h. About 8 g of the ground samples were withdrawn after the grinding for 5, 10, 20 and 50 h.

2.4. Reduction at Atmospheric Pressure

The gasification of carbon, Eq. (2), is extremely endothermic and the overall reaction of the system, Eq. (3), is also endothermic. However, only a few studies[12,13] have quantitatively considered its non-isothermal nature, because of the complexity of the system. To prevent temperature difference in the inside of the sample disks during reactions, sample mass should be as small as possible. Therefore, 30 mg of sample was shaped into thin disks of about 1 mm thickness and 3.8 mm diameter.

The sample disk was put in an alumina or platinum cell of 4 mm inner diameter and 5 mm height. The experimental apparatus for TG-DTA is schematically drawn in **Fig. 1**. Reference material for DTA was αAl_2O_3. Two types of heating operation were employed; (i) with a constant heating rate (constant heating), and (ii) at fixed temperature followed by rapid heating (step heating). Details of these operations are as follows:

(i) Constant heating: The sample and reference in the alumina cells are heated from room temperature to 1 570 K at a rate of 20 K/min.

(ii) Step heating: The sample in the platinum cell is first heated to 620 K and kept for 2 min at this
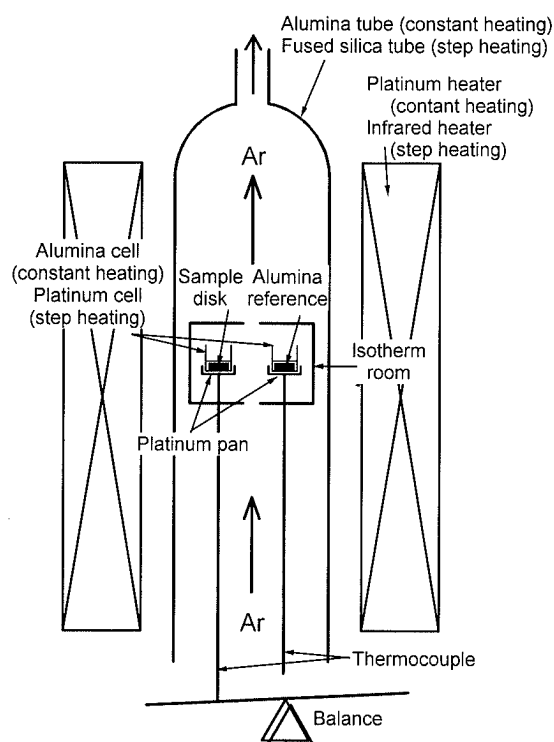
Table 1. Chemical composition of ores A and B. (in mass%)

Sample	T. Fe	FeO	SiO$_2$	Al$_2$O$_3$	CaO	MgO	TiO$_2$	LOI
Ore A	67.4	0.32	0.53	0.88	0.02	0.03	0.05	1.40
Ore B	57.3	0.29	5.02	2.65	0.12	0.09	0.20	9.49

Table 2. Elemental composition of coke and its ash composition. (in mass%)

Elemental composition	Fix. C	N	S	H	Ash
	85.5	1.06	0.50	0.38	9.82

Ash composition	T. Fe	SiO$_2$	CaO	Al$_2$O$_3$	MgO
	15.7	45.7	4.8	22.3	1.7

Fig. 1. Schematic drawing of the apparatus for TG-DTA measurement under atmospheric pressure.

temperature. Vaporization of free water and dissociation of combined water in the ore samples are finalized by this operation. Then, it is rapidly heated up to a target temperature and is kept at that level for 3 min. Target temperatures were varied at 1 370, 1 420, 1 470 and 1 520 K. Time required for the rapid heating from 620 to 1 520 K was approximately 18 s, i.e., about 3 000 K/min in average heating rate. The overshoot at the target temperatures was less than 10 K in all the cases.

Platinum heater + alumina tube and infrared heater + fused silica tube were used for the respective conditions. For the both conditions, the reactions proceeded under Ar stream of 50 N cm^3/min controlled by a mass-flow controller.

2.5. Reduction at High Pressure

The reactions taking place in this system will be influenced by the surrounding pressure, because the rates of carbon gasification, Eq. (2), and reduction of iron oxides, Eq. (1), are obviously dependent on gaseous pressure. To examine the effect of gaseous pressure on the reaction of this system, the TG measurements were conducted in a pressure container made of stainless steel.

The sample disk was placed on a small platinum pan and heated by a platinum heater. The container is of double construction. Outer space is filled with pressurized N_2 and inner room, where the sample is placed, is filled by Ar. The total pressure was varied from 0.1 to 1.5 MPa. The condition of the constant heating was applied to this experiment, but Ar did not flow in this case. To maintain gaseous pressure at a constant level, Ar was discharged at a rate corresponding to the volume expansion due to increasing temperature of the inner room.

2.6. Determination of Standard Conditions

In order to determine a standard mixing ratio and heating rate for the experiments, a series of preliminary experiments were carried out using hematite and graphite reagents.
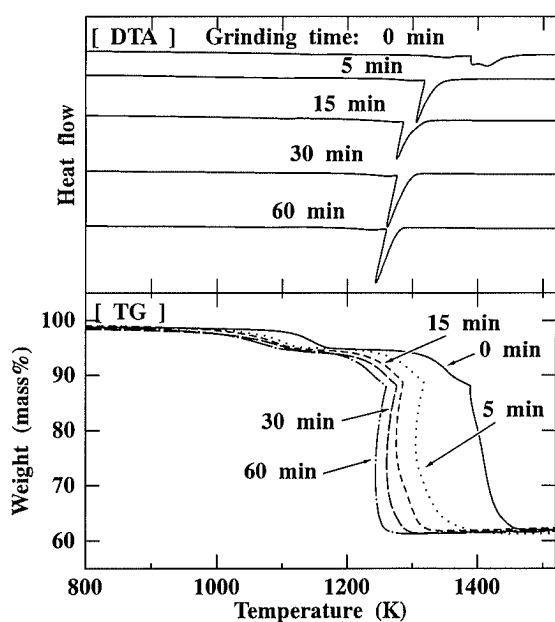
Reagents of hematite, 89.9 mass%, and graphite, 10.1 mass%, which were stoichiometically calculated values on the assumption that all graphite will oxidized to CO_2, were pre-mixed by the above mentioned way and mixed-ground by PM for 5 to 60 min. **Figure 2** shows TG-DTA curves obtained by constant heating. The weight losses at the end of heating, 1 570 K, are almost same for the all samples. From this result, the fractions of CO_2 and CO formed throughout the reaction can be calculated. Mixing ratio of hematite and graphite were determined as 83 and 17.0 mass%, respectively, using the CO and CO_2 fractions so that neither iron oxides nor graphite remained at the end of reaction. For the other samples such as iron ores and coke, the same mixing ratio was applied by ignoring impurities other than carbon and iron oxides. Individual mixing ratios used in this study were listed in **Table 3**.

Furthermore, the reduction experiments were carried out by varying heating rate from 2 to 20 K/min using the pre-mixed sample and samples mixed-ground by PM mill for 60 min. The resultant TG curves are shown in **Fig. 3**. The reaction shifts toward higher temperature with an increase in heating rate. However, since the extent of shift was independent of the mixed grinding time, a standard heating rate was determined as 20 K/min.

2.7. Evaluation of Mixed-ground and Reduced Samples

The samples before and after reduction were subjected to measurements of X-ray diffraction pattern, XRD,

Table 3. Mixing ratio of carbonaceous and iron oxide materials.

Carbonaceous materials	Iron oxide materials	Mixing ratio in mass
Graphite	Hematite	17.0 : 83.0
Graphite	Ore A	16.5 : 83.5
Graphite	Ore B	14.4 : 85.6
Coke	Hematite	19.3 : 80.7
Coke	Ore A	18.8 : 81.2
Coke	Ore B	16.4 : 83.6

Fig. 2. Effect of grinding time on TG and DTA curves for the mixture of hematite and graphite (10.1 mass%).
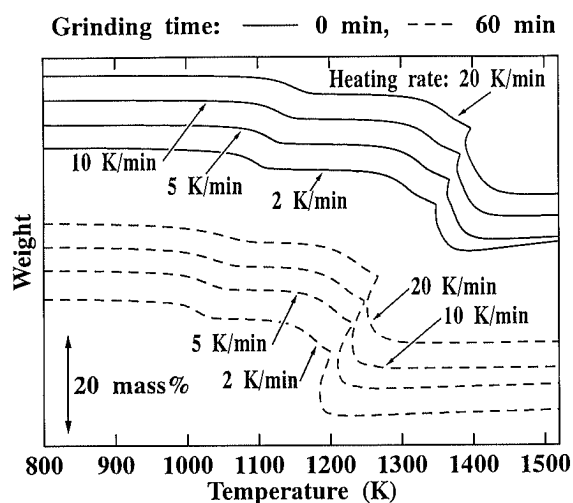

Fig. 3. Comparison of TG curves for hematite and graphite (10.1 mass%) mixture ground by a planetary ball mill for different time.

specific surface area, and optical and scanning electron microscopic observations.

3. Results and Discussions

3.1. XRD and SSA

The XRD patterns for the hematite and graphite mixture mixed ground by PM for different time are shown in **Fig. 4**. The height of peaks attributed to hematite decreases slightly with an increase in grinding time, while the peak of graphite decreases rapidly. This implies that the crystalline structure of graphite is easily deformed and changed into an amorphous state. The slight decrease in hematite peaks may be caused by a decrease in particle size. The same trends were observed for the samples mixed-ground by TM, but it takes more than 200 times longer than those by PM. The coke sample shows an amorphous pattern in the original state. Ore A shows only peak of hematite and ore B hematite and goethite. The peaks observed for both ores decrease slightly with an increase in mixed-grinding time.

Changes in SSA and estimated particle size during mixed-grinding of hematite and graphite reagents by PM are shown in **Fig. 5**. SSA increases rapidly in the early stage and gradually in the later stage. This suggests that particles tend to aggregate in the later stage. At the same time, this implies that formation of composites of hematite and graphite particles takes place and interface area between them increases without apparent size reduction. Mixtures of ore A and coke shows a same trend as that of reagents, although ore A originally has a small value of SSA, $1.47\,m^2/g$. However, SSA of ore B is quite large, $19.4\,m^2/g$, and increased up to about $60\,m^2/g$ during mixed-grinding with coke by PM at 60 min-grinding. This may be because ore B contains many fine open and closed pores, and the closed pores are changed to open ones by the grinding. Mixed-grinding by TM gives a similar change of SSA. However, the mixed-grinding time by TM giving the same value of SSA as that treated by PM is longer by more than 200
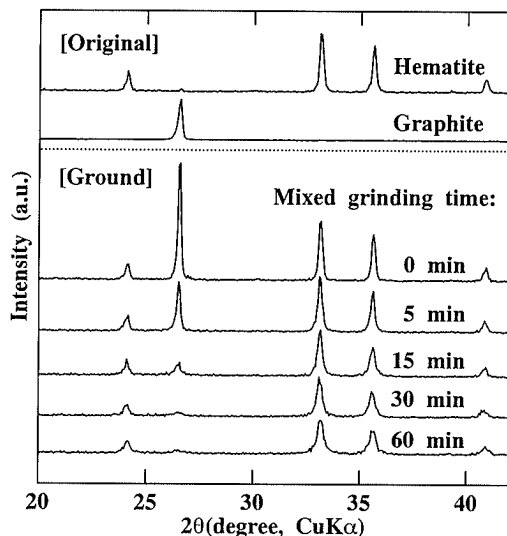
times. This agrees well with the results of XRD.

3.2. Reduction with the Constant Heating

Figure 6 shows TG-DTA curves for the mixture of hematite and graphite reagents mixed-ground by PM for different time. Double endothermic peaks are seen at around $1\,400\,K$ for pre-mixed sample. They are caused by complex reactions Eqs. (1) and (2). However, only one peak appears for the mixed-ground samples. The peak temperature decreases with increase in mixed-grinding time and is about $1\,250\,K$ for the sample of 60 min-grinding. On the other hand, weight losses are observed as three steps in TG curves. These seem to correspond to the reductions of iron oxides; from Fe_2O_3 to Fe_3O_4, to FeO and to Fe, in that order from the lower temperature. There is also a decrease in peak temperature with the increase in mixed-grinding time.

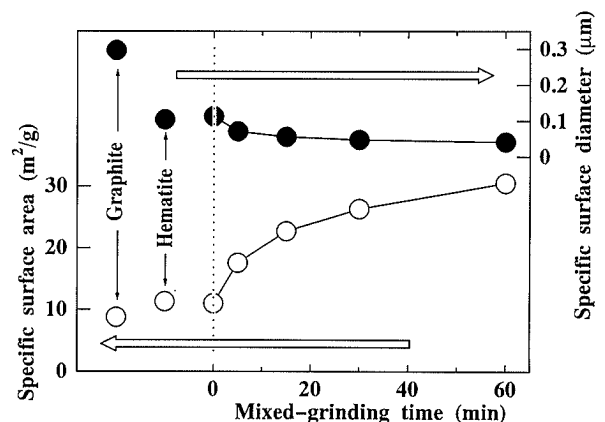The last weight loss, may correspond to the reduction of FeO to Fe, is extremely rapid for the mixed-ground

Fig. 5. Specific surface area and diameter of graphite and hematite reagents and their mixtures ground by a planetary ball mill for different time.

Fig. 4. X-ray diffraction patterns of original and mixed-ground samples of hematite and graphite (17.0 mass%) mixture by a planetary ball mill.
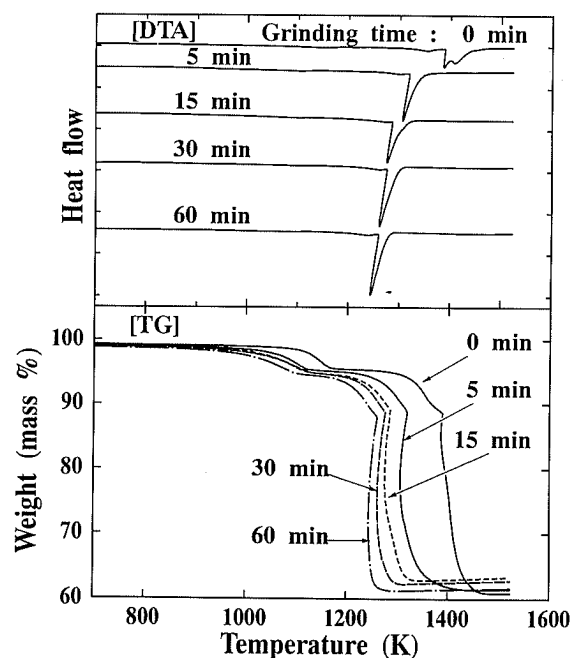
Fig. 6. TG-DTA curves for hematite and graphite mixtures ground by a planetary ball mill for different time.
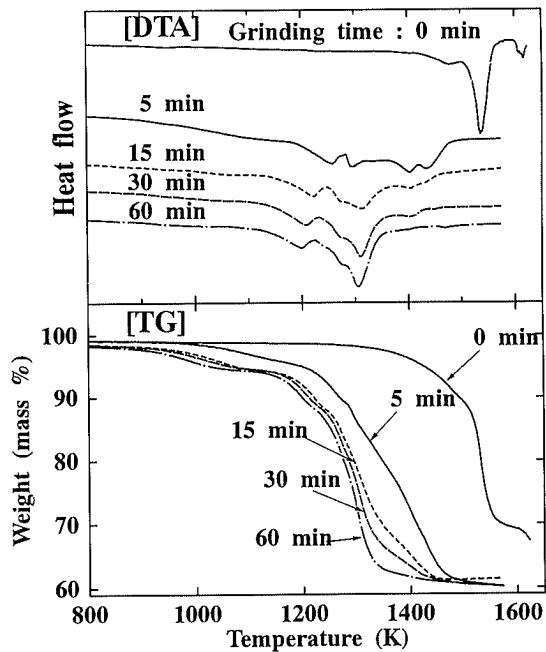
Fig. 7. TG-DTA curves for coke and ore A mixtures ground by a planetary ball mill for different time.
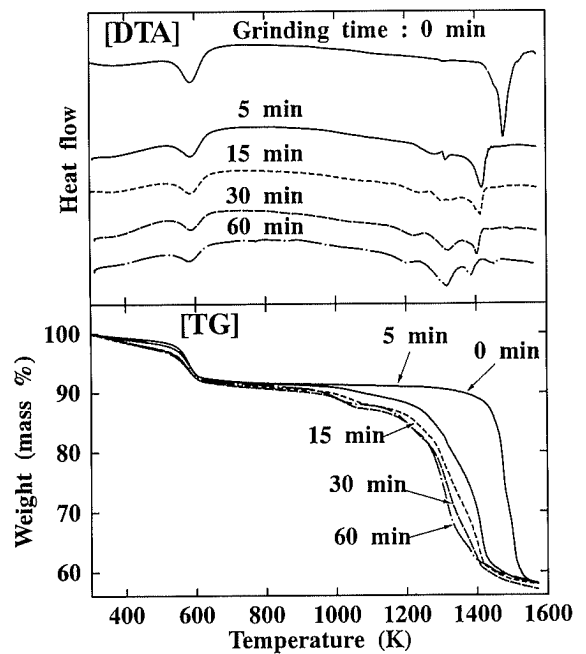

Fig. 8. TG-DTA curves for ore B and coke mixtures ground by a planetary ball mill for different time.

samples and even a certain temperature decrease is seen in the figure. The temperature deviation from pro-grammed pattern is 22 K and time showing such devia-tion is 70 s as maximum values. It is caused by that heat consumption by the reactions exceeds the heat supply from the surroundings. This phenomenon becomes more significant with an increase in mixed-grinding time and suggests that an effect to promote the reactions func-tions during the reduction of iron oxides. A possible explanation is a catalytic effect[1,14,15] of iron produced by the reduction, Eq. (2). Such rapid weight loss can be also seen for the pre-mixed sample. But, it is only at the initial stage and then it becomes slower. This is because the contact area between surface of graphite particles and iron formed on the surface of iron oxide particles is relatively small and therefore the catalytic effect is limited in the initial stage only.

The results for the mixture of ore A and coke mixed-ground by PM are shown in **Fig. 7**. A sharp endothermic peak is seen in the DTA curve for the pre-mixed sample while the peak disappears in the curve for mixed-ground sample and changes into several broad/small peaks between 1 250 and 1 450 K. For the extended mixed-ground samples, the peaks over 1 400 K become small and peak at 1 300 K becomes clearer. Weight of the pre-mixed sample starts to decrease slowly at around 1 350 K and then faster from about 1 520 K. However, the change stagnates again at about 1 540 K. This is likely due to that iron oxide, FeO, reacts with some gangue minerals and it forms compound, for example, fayalite (Fe_2SiO_4),[7] having a low melting temperature since it remains unreduced at such high temperatures. For the mixed-ground samples, the stagnation of weight loss is not seen and the weight loss significantly shifts to lower temperatures. A step reduction is observed in TG curves of the samples mixed-ground for more than 15 min. Rapid decreases in sample weight being ascribed to a

catalytic effect of iron (see Fig. 6) are not seen in this system. Mixed-grinding by TM gave similar results except grinding time is much longer by more than 200 times than PM.

TG-DTA curves obtained for the mixture of ore B and coke mixed-ground by PM are shown in **Fig. 8**. Two endothermic peaks are seen at around 600 and 1 480 K for pre-mixed sample. Since weight decrease is also seen at around 600 K, decomposition of combined water proceeds at this temperature. The peak at 1 480 K corresponds to the gasification of carbon and reduction of iron oxides. The stagnation of the reaction was not observed in this system unlike in the case of using ore A (see Fig. 7) in spite of higher content of gangue minerals in ore B than ore A. A reason of this is that reducibility of ore B is higher because it has many fine pores and pores further form by the decomposition of combined water. The endothermic peak at 600 K becomes small and the decomposition starts at lower temperature with increase in grinding time. The peak at 1 480 K also becomes small and shift to a lower temperature. New peaks appear at 1 200 and 1 310 K for the samples mixed-ground for longer periods.

The combination of materials for preparing composite samples were variously changed and the mixtures were mixed-ground by PM for 60 min. Their TG curves are shown in **Fig. 9**. Rapid weight loss by a catalytic effect of iron is seen in the combinations of "hematite reagent + graphite" and "ore A + graphite" only. The combination of "hematite reagent + coke" shows lower reaction rate than those of "iron ore + graphite". Therefore, gangue minerals and impurities, probably sulfur in coke which is a surface active element, may inhibit the catalytic effect.

3.3. Reduction with the Step Heating

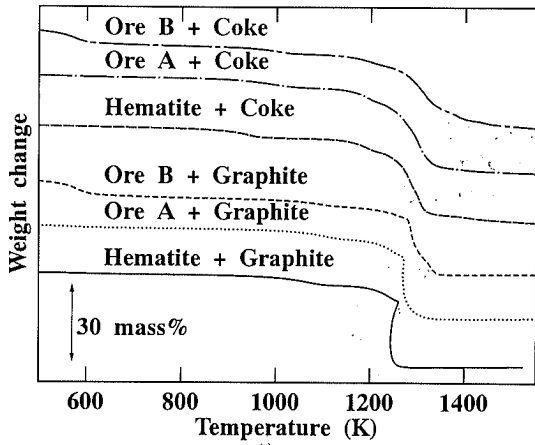Weight changes at 1 420 K in the samples of hematite

Fig. 9. Comparison of TG curves obtained for various combinations of sample mixtures ground by a planetary ball mill for 60 min.
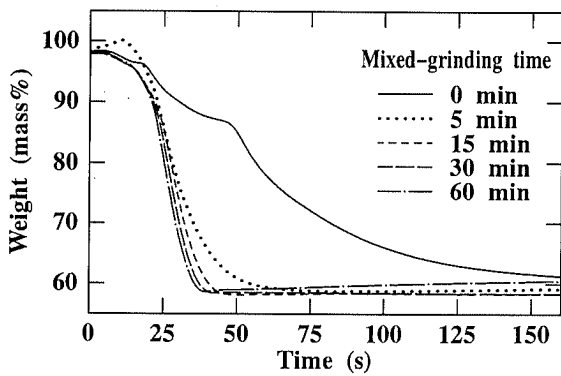

Fig. 10. Change in sample weight with time at 1 420 K for graphite and hematite mixture ground by a planetary ball mill for different time.
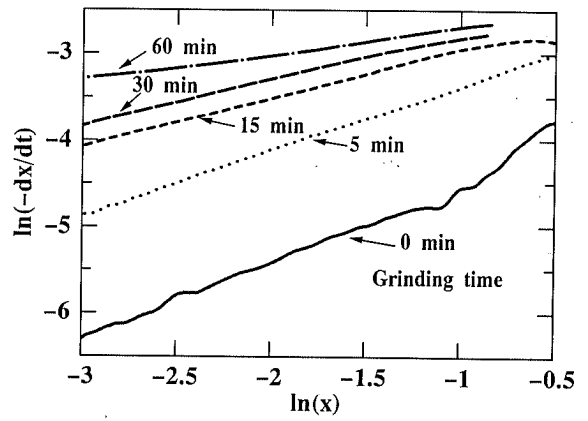

Fig. 11. Relation between $\ln(x)$ and $\ln(-dx/dt)$ at 1 420 K obtained for graphite and hematite mixture ground by a planetary ball mill.

Table 4. Apparent activation energy calculated for the reaction of graphite and hematite mixture ground by a planetary ball mill.

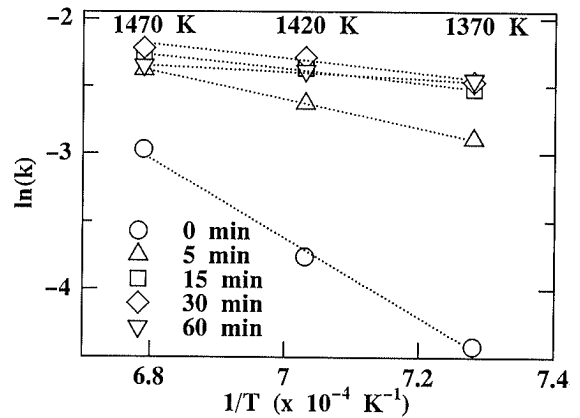| Grinding time (min)	Apparent order of reaction (−)	Apparent activation energy (kJ/mol)	Specific surface area (m²/g)
0	0.853	226	10.3
5	0.740	89.3	17.2
15	0.587	45.7	22.8
30	0.527	47.5	25.3
60	0.307	18.7	29.9

Fig. 12. Relation between $\ln(k)$ and $1/T$ for graphite and hematite mixture ground by a planetary ball mill.

and graphite reagents mixed-ground by PM are shown as a function of time in **Fig. 10**. Weight of the pre-mixed sample decreases in three steps. However, this phenomenon is not clear for the mixed-ground samples and the reaction rate increases with an increase in mixed-grinding time.

The reactions occurring in this system are quite complicated and it is also difficult to estimate diffusion rate of reaction gases through the phases of lower oxides of iron, metallic iron and pores/voids formed by the reaction and heat transfer rate in the sample disk. A simple analysis was attempted by employing a rate equation (Eq. (4))[16] applicable to a reaction of heterogeneous decomposition from solid to gas.

$$-dx/dt = kx^n \quad\quad\quad (4)$$

$$k = A\exp(-E/RT) \quad\quad\quad (5)$$

where, x (−) is ratio of unreacted part, n(−) the apparent order of reaction and $k(\mathrm{s}^{-1})$ reaction rate constant assuming that it follows the Arrhenius equation, Eq. (5). A (s^{-1}) is frequency factor, E (J/mol) apparent activation energy, R (J/mol K) gas constant and T(K) temperature. Equation (4) can be deformed into Eq. (6);

$$\ln(-dx/dt) = \ln(k) + n\ln(x) \quad\quad\quad (6)$$

If a plot of $\ln(-dx/dt)$ vs. $\ln(x)$ calculated from the data

gives a straight line, the rate constant, k, will be obtained by an intercept of the line at $\ln(x)=0$. Further, apparent activation energy, E, can be evaluated by the relation between k and $(1/T)$.

Figure 11 shows relationship between $\ln(-dx/dt)$ and $\ln(x)$ calculated from the result shown in Fig. 10. Fair straight lines are seen in the range of $\ln(x) < -0.7$, i.e., $x<0.5$. In this range, it appears to be that the reduction from Fe_2O_3 to FeO through Fe_3O_4 is completed and that from FeO to Fe proceeds. It can be also considered that the direct reduction, Eq. (3) with $x=y=1$, may occurs when the interface area of FeO and graphite is large. Averaged values obtained as the apparent order of reaction are listed in **Table 4**.

Figure 12 shows relationship between $\ln(k)$ and $(1/T)$

in the range of $0.1 < x < 0.5$. Since all the data follows well straight lines, the analysis is seemingly applicable to this experiment. The values of E calculated from the slopes of the lines shown in Fig. 12 are summarized in Table 4. Value of SSA of each sample is also listed in the table. E suddenly decreases from about 230 kJ/mol for the pre-mixed sample to 90 kJ/mol for the sample mixed-ground for 5 min. Then, it further decreases with an increase in mixed-grinding time. The value of E for the sample mixed-ground for 60 min gives quite small value, about 19 kJ/mol.

Although it would be misleading to discuss details of the reaction based on this simple analysis, such decrease in the apparent activation energy suggests that promotion of gasification of carbon and/or change of rate limiting step of the reactions occur by the mixed-grinding.

3.4. Reduction at High Pressure

Mixture of hematite and graphite reagents mixed-ground by PM were subjected to reduction experiments at constant heating rate under 1.0 MPa of argon atmosphere. Obtained TG curves are shown in **Fig. 13**. Reaction temperature decreased with increase in mixed-grinding time. This trend is similar to that of reaction under an atmospheric condition, while the reaction temperatures are relatively lower for the all mixed-grinding time. TG curves obtained by varying total pressure for the sample mixed-ground for 60 min are shown in **Fig. 14**. Reaction temperature decreased with an increase in pressure. The other samples with different mixed-grinding time gave similar results.

If iron oxides are supposed to reduce simply by CO in this experiment as Eq. (1), chemical reaction rate will increase with total pressure since increase in total pressure will lead to an increase in partial pressure of CO. Hence, the reduction rate increases with an increase in total pressure when the particle size of iron oxides is as small enough as that mass transfer rate within the particles does not affect the total reduction rate. However, the solution loss reaction Eq. (2), which have been reported as a rate-limiting step by many authors, and the reduction of iron oxides by solid carbon, Eq. (3), are suppressed by an increase in total pressure. Further, since the
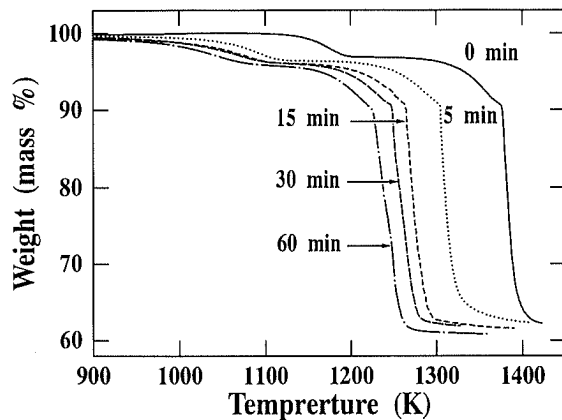
solution loss is a large endothermic reaction, a certain temperature decrease of the sample disk is unavoidable even for the present case. Total pressure also influences retention time of reaction gases and heat diffusivity in the sample disk. The present study did not examine such complicated effects of total pressure on reactions/phenomena in detail and it will be a subject for future studies.

3.5. Structure of Samples after Reduction

Figure 15 is the optical microscopic photos of cross sections of the sample disks reduced at constant heating rate. These were prepared by the mixture of hematite and graphite reagents: (a), (b) pre-mixed sample and (c), (d) sample mixed-ground by PM for 60 min. The pre-mixed sample after reduction shows a porous structure of iron while the mixed-ground sample is
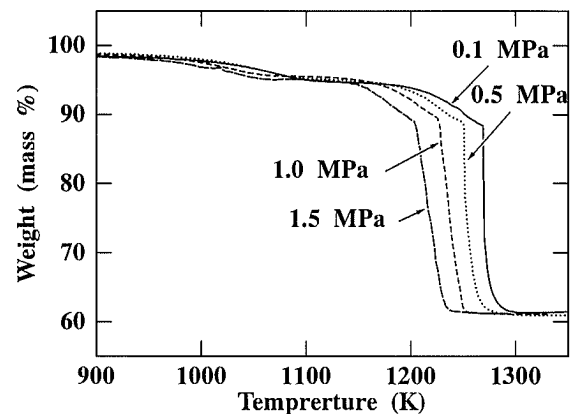

Fig. 14. TG curves obtained under different Ar pressure for graphite and hematite mixture ground for 60 min.
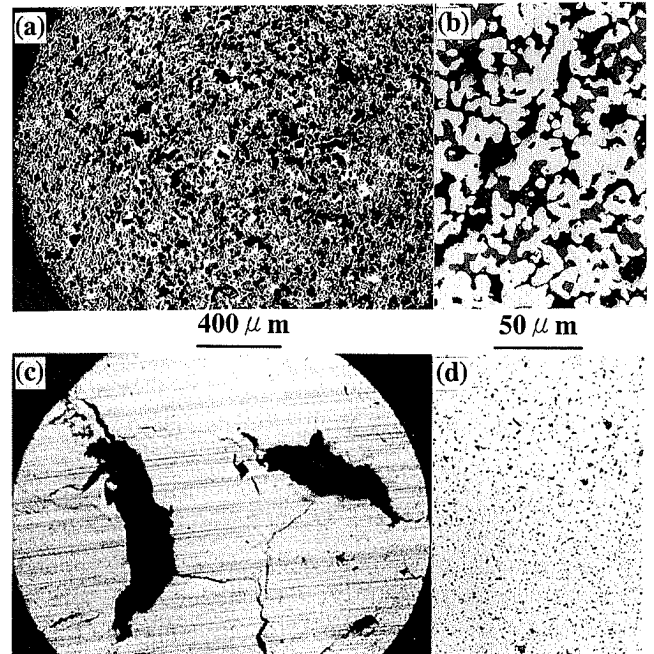

Fig. 15. Sectional photos of sample disks after reduction with constant heating rate, prepared by pre-mixed graphite and hematite reagents and those mixed-ground for 60 min.
((a), (b): Pre-mixed sample, (c), (d): Mixed-ground sample)

Fig. 13. TG curves obtained under 1.0 MPa of Ar pressure for graphite and hematite mixture ground by a planetary ball mill.

relatively dense except that a few cracks and large voids exist. Small gray phases are studded in the former (Fig. 15(b)). These were identified by EPMA as wustite phases which remained unreduced. The latter has few wustite phases and seems to have shrunk due to sintering effect. Such structural difference is thought to be mainly caused by differences of particle size and extents of mixing and complexity of the mixed-ground samples. The samples reduced by the step heating gives a similar tendency to the above, while their densities are relatively low because the reaction time is comparably short. More cracks are observed in the reduced sample disks mixed-ground for longer time.

Pressure of the inside of the sample disk increases during reaction because of formation of reaction gases and increase in temperature.[17] Diffusion of formed gas tends to be blocked by the dense structure of iron. The cracks may explosively propagate when the structure cannot withstand the gaseous pressure. On the other hand, oxidation rate of the iron phase having such dense structure is estimated to be fairly small. This is note-worthy in a practical operation since it suggest that the re-oxidation of products can be prevented.

A phase containing sulfur was observed for the samples prepared using coke. The maximum concentration is about 1 mass%. This may form by concentrating sulfur in coke as FeS. However, we did not find a significant characteristics of distribution of such phases. Behavior of sulfur and its effect on the reactions are remained as future subjects.

4. Conclusions

The effect of mixed-grinding of iron oxides and carbonaceous materials on the reactions in high temperatures were examined under various conditions. The mixed-grinding was conducted using planetary and tumbling ball mills. Reaction rate was mainly measured by a TG-DTA method in argon atmosphere applying different heating pattern and total pressure. The results are summarized as follows:

(1) Mixed-grinding operation significantly increases reaction rate, in other words, decreased reaction tem-perature.

(2) Iron produced through reduction of iron oxides seems to function as a catalysis to the gasification of carbon by CO_2. However, the catalytic effect is inhibited when using coke and iron ores instead of reagents of graphite and hematite. It may be attribute to gangue minerals and/or impurities, especially sulfur in coke.

(3) A simple kinetic analysis was attempted assuming a heterogeneous decomposition from solid to gas. The apparent activation energy obtained from the analysis considerably decreases with progress of mixed-grinding. It suggests that gasification of carbon is promoted through enhancement of the catalytic effect of iron and/or rate limiting step changes from the gasification of carbon to the direct reactions between iron oxides and carbon.

(4) Increase in total pressure leads to decrease in reaction temperature. Further, the effect of mixed-grinding on the reactions in higher total pressure is similar to that in atmospheric pressure.

(5) Mixed-grinding gives a dense structure of reduced sample. Oxidation rate of such dense iron phase is estimated to be small.

REFERENCES

1) K. Otsuka and D. Kunii: *J. Chem. Eng. Jpn.*, **2** (1969), 46.
2) K. Rao: *Metall. Trans.*, **2** (1971), 1439.
3) H. Ree and M. Tate: *Tetsu-to-Hagané*, **57** (1971), 465.
4) E. T. Turkdogan and J. V. Vinters: *Metall. Trans.*, **3** (1972), 1561.
5) T. Shimazaki, M. Ikeda and T. Morimune: *Tetsu-to-Hagané*, **59** (1973), 17.
6) N. S. Srinivasan and A. K. Lahiri: *Metall. Trans. B*, **8B** (1977), 175.
7) R. J. Fruehan: *Metall. Trans. B*, **8B** (1977), 279.
8) S. Mookherjee, H. S. Ray and A. Mukherjee: *High Temp. Sci.*, **21** (1986), 119.
9) T. Sharma: *Ironmaking Steelmaking*, **19** (1992), 372.
10) P. Tiwari, D. Bandyopadhyay and A. Ghosh: *Ironmaking Steelmaking*, **19** (1992), 464.
11) S. K. Dey, B. Jana and A. Basumallick: *ISIJ Int.*, **33** (1993), 735.
12) B.-H. Huang and W.-K. Lu: *ISIJ Int.*, **33** (1993), 1055.
13) S. Sun and W-K. Lu: *ISIJ Int.*, **33** (1993), 1062.
14) D. Bandyopadhyay, N. Chakraborti and A. Ghosh: **64** (1993), 340.
15) M. C. Abraham and A. Ghosh: *Ironmaking Steelmaking*, **6** (1979), 14.
16) E. S. Freeman and B. Carroll: *J. Chem.*, **62** (1958), 394.
17) T. Shimazaki: *Tetsu-to-Hagané*, **71** (1985), 1751.