Intensive Improvement of Reduction Rate of Hematite–Graphite Mixture by Mechanical Milling

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The effect of ball milling of raw materials on the reaction behavior of composite mixture of hematite and graphite have been studied. Hematite was mixed with 19.84 wt% graphite (C/O ratio was 1.1 in composite mixture) and subjected to ball milling. The milling time was changed from 6 to 100 hr with the hematite–graphite mixture. On the other hand, graphite or hematite was milled alone and then mixed with non-milled hematite or graphite, respectively. The effect of milling time on reduction process in an Ar atmosphere was studied by TG-DTA. The samples were heated by a constant heating rate of 10°C/min from room temperature up to 1 100°C and maintained for 30 min at this temperature.

The rate of reaction (RTG) was obtained by the differentiation of weight loss curve. It was found that the RTG curve consisted of three reaction curves which were hematite–magnetite (HM), magnetite–wustite (MW) and wustite–metallic iron (WF) reductions. The curve corresponding to the HM reduction located in low temperature range and stood alone from other two reduction curves (MW and WF reductions). The curves of MW and WF reductions were overlapped. The pulse-like reduction curve corresponding to WF reduction was observed in the longer milling time, which meant extremely high rate of reduction.

The temperatures decreased and the reaction degrees at each peaks increased with increasing milling time.

The kinetic analysis applying the single and consecutive reaction was carried out. The calculated reaction curves were in good agreement with the observations which showed that the reaction mainly occurred in this system was the solid oxide–solid carbon reaction. The variation of parameters of rate constant presented the different mechanism of reaction between shorter and longer milling time at the border of 24 hr.

KEY WORDS: rapid reduction; hematite; graphite; composite pellet; mechanical milling; ball milling; reduction; carbothermic reduction.

1. Introduction

For almost a century, the reduction process of iron oxides with carbonaceous materials has been studied by many investigators.[1-7] The most of these researchers have studied the kinetics and mechanism of reactions between iron oxides and solid carbon. The initiation of reaction must be the direct reaction between the iron oxide and solid carbon especially in an inert atmosphere (Case I: Reaction (1)), although the following mechanism in which the product gases were related to the overall reaction was generally accepted (Case II: Reactions (2) and (3)).,

Case I: $Fe_xO_{y(s)} + C_{(s)} = Fe_xO_{y-1(s)} + CO_{(g)}$ ....(1)
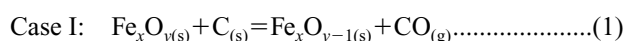
One might be able to imagine that once the Reaction (1) proceeded, the interface between the oxide and solid carbon was separated. In such a situation, the reaction should be proceeded by the gaseous products (Case II).

Case II: $Fe_xO_{y(s)} + CO_{(g)} = Fe_xO_{y-1(s)} + CO_{2(g)}$ ....(2)

$C_{(s)} + CO_{2(g)} = 2CO_{(g)}$ ....(3)
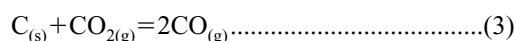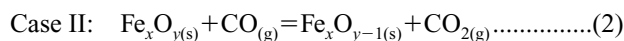
No matter what the real reaction mechanism is, the overall reaction can be presented by Reaction (1) and it is the most difficult point for studying this system. The extent of reaction mechanisms, case I and/or case II will change complexly with the conditions of the composite mixture as follows.

- Macroscopic Features
  - (a) kinds of raw materials (iron ore, reagent hematite, coke, graphite, *etc.*)
  - (b) density of mixture (depending on the compressed pellet or cement bonding)
  - (c) diameter of pellet
- Microscopic features
  - (d) particle size and its distribution of oxide and carbon
  - (e) contact area between oxide and carbon (geometric area)
  - (f) state of contact (distance between the oxygen in oxide atom and carbon atom)
  - (g) state of crystal (amorphous or crystalline particle, especially graphite has different reactivity)

Consequently, these conditions will control three factors,

chemical reaction, heat transfer and gas diffusion, directly and indirectly.

For example, in the case of pellet having large size, the evolved gas (CO and CO_2) will diffuse to the outside of pellet and the possibility of gas–solid reactions (Reactions (2) and (3)) will increase in the course of diffusion as a function of the size and density of pellet. Such a macroscopic feature of mixture as well as microscopic one will affect strongly the reaction mechanism.

The mechanical milling will also change the microscopic features ((d), (e), (f) and (g)). Especially, the contact area (e) and the state of contact (f) should be different from the milling conditions (milling energy: rotation speed and weight of balls, milling time, *etc*.) When the real contact between carbon atom and oxygen atom in the oxide could be attained, it would be the same as a chemical reaction. Actually in this experiment, the CO evolution was confirmed during milling, which meant that the reduction reaction must be occurred. More or less, many state of contact would exist during milling and the reactivity of the product would be different significantly from the milling condition.

In this study, just a mechanical milling (planetary ball milling) was carried out and the milled sample (20 mg) without compressing was used for TG-DTA experiment, in which the reaction mechanism, Case I would govern mainly the system.

In the case of second mechanism (Case II), as the rate of carbon gasification reaction (Reaction (3)) at temperature below 1 100°C is considerably lower than the rate of reduction reaction of iron oxides, the overall rate is controlled by the carbon gasification reaction at temperature below 1 100°C.[8] However, at higher temperature the rate of Reaction (3) increases rapidly and the controlling mechanism of overall rate would be changed and the overall rate of reduction reaction is to be controlled by both Reactions (2) and (3) proceeding in series.

On the other hand, a great deal of experiments has been performed and many attempts have been done to develop new direct reduction processes by using solid carbonaceous materials and iron ore composites. FASTMET is an example of such processes. Also, some affecting factors, such as the type of carbonaceous materials and iron oxide, the ratio of oxygen to carbon in composite mixture, the particle size of starting materials, additive materials and process conditions have been studied. With regard to this, in recent years, some experiments have been performed in order to study the effect of mechanical treatment, *i.e.* grinding or ball milling of raw materials on reduction process.[8–10] Some of these experiments have been done by mixing of raw materials after preparing of each one separately by individual milling and obtaining the desired particle sizes. Many investigations have also been performed to study the effect of mechanical ball milling treatment on iron oxides or graphite individually.[10,11] The experiments that studied the effect of mixed grinding or ball milling of raw materials on reduction process are less, and many aspects of the process are remained unclear yet. In the present work, authors studied, in more details, the effect of ball milling of raw materials on the reduction behavior of hematite by pure graphite. Reduction experiments were done in an argon atmosphere using TG-DTA. The reaction mechanism was classified into

three reactions (hematite, magnetite and wustite reductions) and kinetic analysis was carried out for each reduction curve.

2. Experimental

Reagent grade of hematite ($>99\%$ Fe_2O_3) and high purity graphite with high density (1.77 g/cm^3) and low ash content (<100 ppm) were used as starting materials. The graphite was crushed into powder roughly at first and the powder was sieved and the $-100\,\mu$m fine graphite was used in mechanical milling (planetary ball milling). Reaction process (reduction and carbon gasification) was studied by DTA and TG experiments using TG-DTA device (sample weight: 20 mg, resolution: 1 μg). The crucible was made of platinum and 4 mm inner diameter and 3 mm depth. Gas leakage into the reaction system will affects the reaction kinetics, especially oxygen from air increases the weight loss of carbon significantly. In this experiment, original analyzer was modified and the gas-tight flowing system was developed. The weight loss of pure graphite in Ar atmosphere was less than 1.0%, which was almost the same amount of weight loss from the reaction with remained oxygen in Ar and originally adsorbed oxygen in the graphite. The mixture of hematite and graphite with a fixed composition (19.84 wt% C in hematite, which corresponds to C/O=1.1) was subjected to ball milling and the milling time was varied from 6 to 100 hr. The milling treatment was performed in a Fritsch Pulverisette 6 planetary ball mill. A ceramics (Alumina) vial of 500 cm^3 volume, charged with 10 alumina balls of a nominal diameter of 20 mm, was used as the milling medium in all the experiments. The rotating speed of the vial was maintained constant at 200 rpm. The weight ratio of powder to balls was 1 : 5. After the desired time intervals, a small amount of powder was sampled for the reduction experiment (TG-DTA) and the remained powder was served for the following milling. TG-DTA experiments were conducted under an Ar atmosphere with a constant flow rate of 50 Ncc/min and without any compression. Samples were heated with a constant heating rate of 10°C/min from room temperature up to 1 100°C and kept at this temperature for 30 min.

In other experiment for comparison, the single hematite or graphite was milled and mixed with non-milled graphite or hematite in the same weight ratio (C/O=1.1) and the mixture subjected to reduction test at the same conditions as explained above. The method of mixing between non-milling and milling sample was simple and just a spoon was used for mixing in a beaker. If a mortar and a pestle were used for mixing, a similar effect as milling would be added to the sample. The mixing time with a spoon was changed from a few minutes to several ten minutes and these samples were examined with TG-DTA. However, the reaction degree was almost the same and could not reach 100% for H72. Furthermore, the compressing effect of sample on the reduction degree was examined. There was little effect of compressing of sample (G100 or H72) on the reduction degree.

The notations of samples in different conditions were determined for convenience as shown in **Table 1** (*e.g.* HG100: hematite and graphite mixture was milled for 100 hr, G100:

Table 1. Notation of sample mixtures in different conditions and theoretical weight loss of sample and observed one.

Notation	Milling condition H: hematite G: graphite		W0 (mg)	W1 (mg)	−ΔW (mg)	TGLmax −ΔW/W1 (%)
					observed	observed
HG6	6 hours	(mixed before milling)			4.066	48.23%
HG24	24 hours	(mixed before milling)			7.946	94.26%
HG72	72 hours	(mixed before milling)			8.428	99.98%
HG100	100 hours	(mixed before milling)	20.0	8.430	8.577	101.75%
H72	Hematite:72hours Graphite: 0hour	(Mixed after milling)			4.263	50.57%
G100	Hematite: 0hour Graphite: 100 hours	(Mixed after milling)			8.232	97.66%

W_0: total weight of sample (Fe_2O_3+C) before exp. $W_1=[O]_0+[C]_0=$ 8.430 mg, (O/C=1.0), $[O]_0$: reducible oxygen, $[C]_0$: fixed carbon in graphite

Fig. 1. Typical results of TG-DTA for the mixture of hematite and graphite after milling for 100 hr (HG100). (TGL: weight loss curve, RTG: rate of weight loss, DTA: temperature difference between reference and sample, Temp.: heating profile)

graphite was milled for 100 hr and mixed with non-milled hematite).

The main subject of this study is to clarify the reaction rate of the mixture made by the mechanical milling. However, it would be very important to know the state of particles (particle size and contact area, *etc.*) before and after milling. We carried out the analyses of the particles using XRD, SEM and TEM. Furthermore, gas analysis was carried out using the atmosphere-controlled vial. It was found that the complicated phenomena occurred during the milling and the details will be published in the subsequent paper. Because this paper is focusing on the reaction behavior of the mixture made by the mechanical milling, some results (SEM images of particles before and after the milling and some results of XRD) related to the state of particle were shown in Appendix.

The results obtained by XRD, SEM and TEM analyses, which will be published in the subsequent paper, are summarized as follows.

(a) Reduction occurred during the milling under argon atmosphere using the atmosphere-controlled vial (the packing of cap of vial was modified by authors for gastight vessel).

(b) Reoxidation occurred during the milling under air atmosphere, when the commercial vial having less gastight cap was used. The crystal size of hematite was almost the same during the milling because of reoxidation. On the other hand, the crystal size of graphite decreased.

(c) When the single hematite sample was milled, the crystal size decreased with the increasing milling time.

It could be considered that the reduction and the reoxidation of iron oxide might be repeated during the milling in the air. As the less-gastight vial was used in this study, the oxygen partial pressure inside the vial was almost the same as the air. From this mechanism, the crystal size of hematite in the mixture would be almost the same, which was confirmed by XRD (Appendix) and SEM. Although the size of hematite crystal was the same in the course of milling, the state of contact (not only the geometric contact area but also the distance between the oxygen (or iron oxide) and
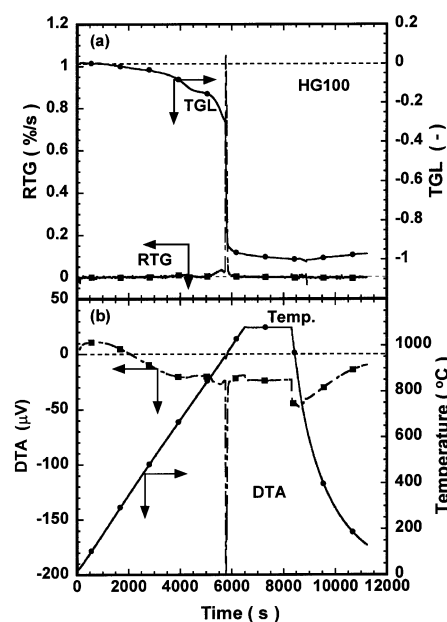
the carbon) between hematite and graphite could be changed and closed. If the contact between the hematite and graphite was loose, the interface would be separated easily, when the reaction proceeded. Such situation might occur in the samples, H72 and HG6, whose reaction degrees were not reached 100%.

Especially in the milling of single hematite, sometime reagent grade sample is very fine and easy to agglomerate during the milling,. The hematite sample adhered to the wall of vial and made a thick layer. Since the effect of milling did not work on the sample in a long time milling, the layer on the wall was broken at a given time interval (2 hr). The crystalline size of reagent hematite was from 1 to 9 μm before milling and the size of crystalline decreased to around 0.1 μm or less in 26 hr (Appendix).

3. Results and Discussions

The typical TG-DTA curves of the sample after 100 hr milling (HG100) are shown in **Fig. 1**. The definition of TGL (weight loss of sample) and RTG (rate of weight loss) are as follows:

$$TGL=\frac{-\Delta W}{W1} \quad \text{...........................(4)}$$

$$RTG\,(\%/s)=-\frac{d(TGL)}{dt}\times100=\frac{d(\Delta W/W1)}{dt}\times100 \quad ....(5)$$

where ΔW means the change of weight from the beginning of experiment and $W1$ means the initial weight of reducible oxygen and fixed carbon after milling in the mixture and the detail of $W1$ will be explained in the next paragraph. To get a smooth curve of RTG, the smoothing of TGL curve was performed and the differential calculation of TGL curve in the adequate regions according to the curvature was conducted. When the variation of curve is monotonous,

the longer differential region will be adequate for the reduction of noise. The shorter region should be taken for a rapid phenomenon, otherwise the sharp change of curve will be moderated. One example for smoothing treatment was shown in Appendix (Fig. A4). The period for numerical differentiation was 100 to 500 s for the region of HM and MW reductions and was about 1 to 5 s for WF reduction.

Figure 1(a) shows the variation of TGL and RTG during heating up experiment. The temperature profile is shown in Fig. 1(b). The point of inflections would correspond to the different stage of reduction and the quite rapid weight loss at the stage of wustite to metallic iron (W–Fe) was found, which was prominent with the increasing milling time. Corresponding to the quite high rate of reaction, the rapid and large heat flow (DTA (μV)) was observed, which meant the large endothermic reaction (Fig. 1(b)). The curve of DTA in Fig. 1(b) was not corrected from the base line shift, and then the reference experiment was carried out with a empty Pt crucible and the all data from DTA was corrected the base line shift in the later section.

The overall reaction in the present study can be expressed as follows, if there is no reaction with product gas:

$$Fe_2O_3 + 3C = 2Fe + 3CO \quad\text{.........................(6)}$$

When the mixture before experiment contains 1 mol Fe_2O_3 and 3 mol carbon, the percentage of carbon is 18.40 % in the mixture, in which the mole ratio of oxygen to carbon is 1.0. In this experiment, slightly excess carbon content (19.84 mass%, C/O=1.1) was adopted to compensate the consumption from the gas–solid reaction. As the weight loss of sample mixture corresponds to the loss of oxygen in hematite and fixed carbon in graphite, the maximum weight loss can be calculated in the assumption of Reaction (6) and the results are shown in Table 1, where $W0$ means the weight of sample before experiment ($Fe_2O_3 + C$), $W1$ means the maximum weight loss ($[O]_0 + [C]_0$ (mg)) of sample at the end of reaction, when the Reaction (6) is assumed, ($[O]_0$; initial reducible oxygen (mg), $[C]_0$; fixed carbon (mg)). However, the reactions actually occurred can not be understood only from the percentage of weight loss, and a precise gas analysis will be necessary to determine the kind of reaction. In this study, based on the assumption of Reaction (6), the reaction curves were re-calculated with the obtained rate constants. Finally, the reaction heats for each reaction were evaluated and compared with the obtained DTA data. Because the reduction with solid carbon accompanies by the large endothermic reaction and the reduction (hematite and wustite) by CO gas shows the exothermic reaction (the details are shown in Sec. 3.3).

It was found the observed weight losses of the mixture increased with the milling time from 6 to 100 hr. When H72 and G100, which hematite or graphite are milled separately and mixed with non-milled graphite or hematite, were compared, the final weight losses were 50.57 mass% in H72 and 97.66 mass% in G100. This result means that the reactivity of carbon affects the reaction significantly. As the longer milling time of graphite increases the larger amount of amorphous carbon which has a higher reactivity, the degree of reaction (weight loss) increases with increasing milling time.[12] If the Reactions (2) and (3) occurred during experiment, the maximum weight loss would never exceed the
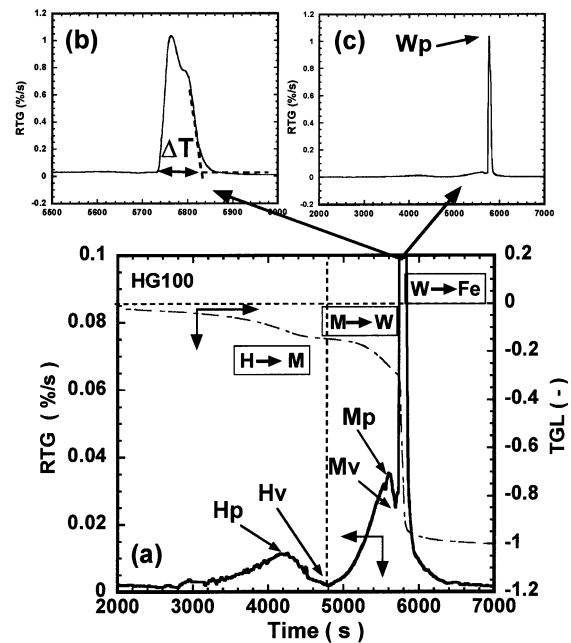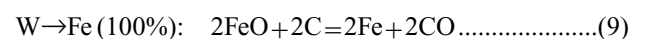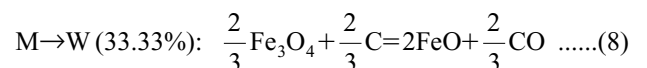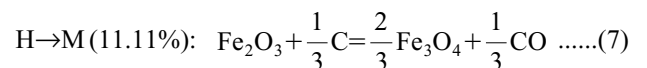

Fig. 2. Details of RTG curve and definitions of characteristic points.

100 mass% ($\Delta W/W1$). Since the temperature was lower than 1 100°C, the observed weight loss meant that the portion of gas–solid reactions (Reactions (2) and (3)) must be very small in present experiment. In author's laboratory, gas analysis using QMS (quadrupole mass spectrometer) was performed for the reaction of composite pellet with 20 mm in diameter and 10 mm in height. The CO_2 evolution was confirmed during experiment and the mole ratio of CO to CO_2 was from 1:1 to 1:2. However, the ratio decreased with the diameter of pellet, which meant the efficiency of gas–solid reaction decreased with the length of path of gas diffusion. On the other hand, in this experiment, the weight of sample mixture was only 20 mg without compression (apparent density in the crucible was about 0.5 g/cm³). From these reason, the situation about gas–solid reaction might be different from the result of Kasai *et al.*[8]

As the gas–solid reaction would be negligibly small, the analysis was carried out with the assumption of Reaction (1).

The actual reaction of 1 mol Fe_2O_3 will proceed as follows:

$$H{\to}M\,(11.11\%):\quad Fe_2O_3 + \frac{1}{3}C = \frac{2}{3}Fe_3O_4 + \frac{1}{3}CO \quad\text{......(7)}$$

$$M{\to}W\,(33.33\%):\quad \frac{2}{3}Fe_3O_4 + \frac{2}{3}C = 2FeO + \frac{2}{3}CO \quad\text{......(8)}$$

$$W{\to}Fe\,(100\%):\quad 2FeO + 2C = 2Fe + 2CO \quad\text{....................(9)}$$

As the reaction degrees of mixture are 11.11, 22.22 and 66.67 % at each reduction stage from Reactions (7), (8) and (9), respectively, the weight losses of sample from the beginning of experiment are 11.11, 33.33 and 100.0 %. **Figure 2** shows the details of RTG curve in HG100 as a typical example. When the RTG curve was magnified in the low range, the three kinds of peaks in convex curves could be confirmed in all experiments. The characteristic points of each convex curves were defined for the comparison of
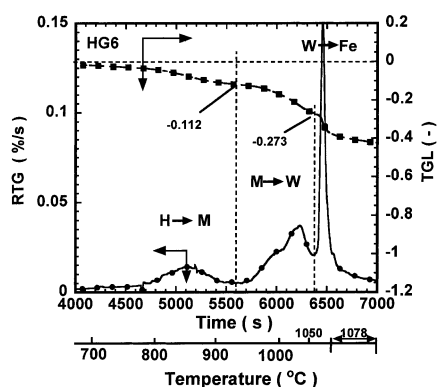
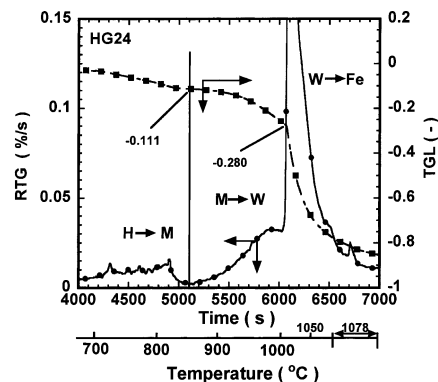**Fig. 3.** Variations of TGL and RTG curves for HG6.

Fig. 4. Variations of TGL and RTG curves for HG24.
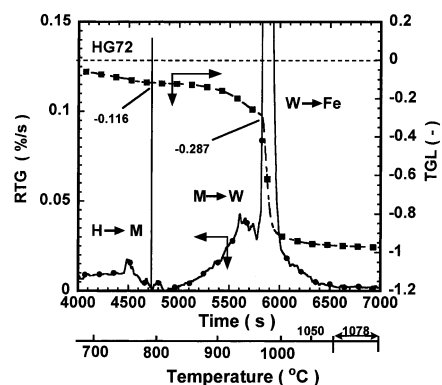

Fig. 5. Variations of TGL and RTG curves for HG72.
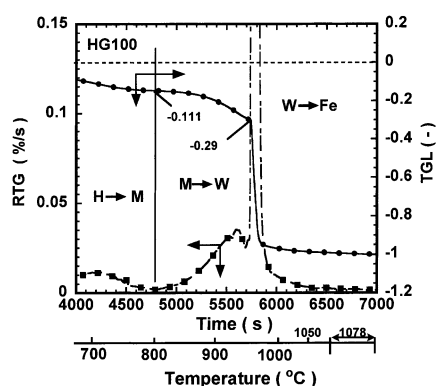

Fig. 6. Variations of TGL and RTG curves for HG100.
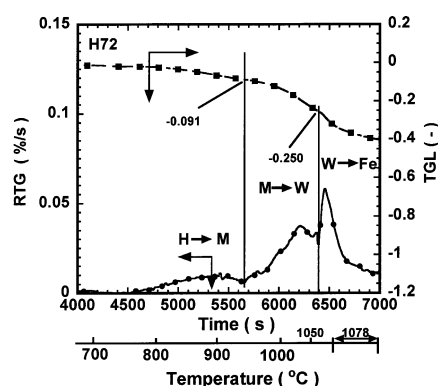

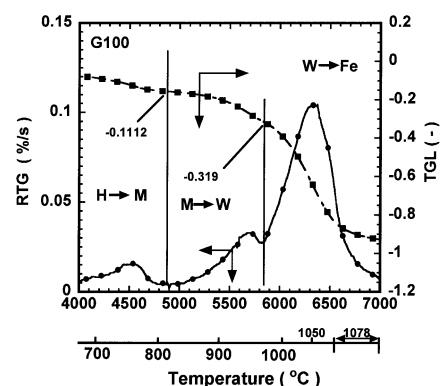
Fig. 7. Variations of TGL and RTG curves for H72.

Fig. 8. Variations of TGL and RTG curves for G100.

Table 2. Characteristic points of reaction curves (RTG).

| Notation of Sample | Hp | | | Mp | | | Wp | | | TGL x100(%) at Hv | TGL x100(%) at Mv | ΔT |
	Temp. (°C)	TGL x100(%)	RTG (%/s)	Temp. (°C)	TGL x100(%)	RTG (%/s)	Temp. (°C)	TGL x100(%)	RTG (%/s)			(°C)
HG6	859	8.46	0.0133	1037	23.6	0.037	1071	32.8	0.150	11.2	27.3	18.7
HG24	817	9.90	0.0141	982	22.5	0.0325	1008	35.5	0.300	11.1	28.0	56.7
HG72	756	10.3	0.0120	934	21.3	0.0404	963	41.5	0.797	11.6	28.7	26.8
HG100	710	11.2	0.0113	930	26.4	0.0349	941	46.6	1.035	11.1	29.0	13.1
H72	897	6.62	0.0098	1029	19.5	0.0374	1070	29.5	0.058	9.1	25.0	39.3
G100	758	12.6	0.0148	948	28.2	0.0325	1047	64.9	0.103	11.1	31.9	132

results among the different conditions. In Fig. 2, the notations Hp, Mp and Wp express the positions of peaks of respective reaction curves and Hv and Mv express the positions of valleys between Reactions (7) and (8) and between Reactions (8) and (9), respectively. The last peak of wustite to metallic iron reduction (W→Fe) was always biggest one and the curve was quite sharp especially in the longer milling time. The width ΔT shown in Fig. 2(b) can be another characteristic factor on the phenomenon which will correspond to the period of the reduction completed at the last stage of reduction.

3.1. Features of Curve Corresponding to Hematite to Magnetite (HM) Reduction

Figures 3 to **8** show the curves of TGL and RTG in the TG-DTA test using the samples of HG6, HG24, HG72, HG100, H72 and G100, respectively.

The temperature and TGL at peak for the first convex curve corresponding to the hematite–magnetite (HM) reduction was lowest in comparison with other two peaks and the temperature range was from about 500 to 930°C depending on the milling time. The curve for HM reduction was separated from other two curves. The values of TGL at Hv for the HG6, HG24, HG72 and HG100 were almost 11.11%, which corresponds to the end of HM reduction (**Table 2** and **Fig. 9**(a)). The temperature at Hp decreased with increasing milling time from HG6 to HG100 (Fig. 9(c)) and the TGL at Hp showed slightly increase from HG6 to HG100. In the case of H72, which only hematite was milled, it was found that HM reduction was lowest and overlapped with MW reduction (Fig. 7). The temperature at Hp of H72 was also highest (897°C , Table 2 and Fig. 9(c)). On the other hand, in G100, the temperature at Hp is very low and 758°C which was closed to HG72. In comparison of first curve (HM reduction) between H72 and G100, it was obvious that the reactivity of carbon had quite large ef-
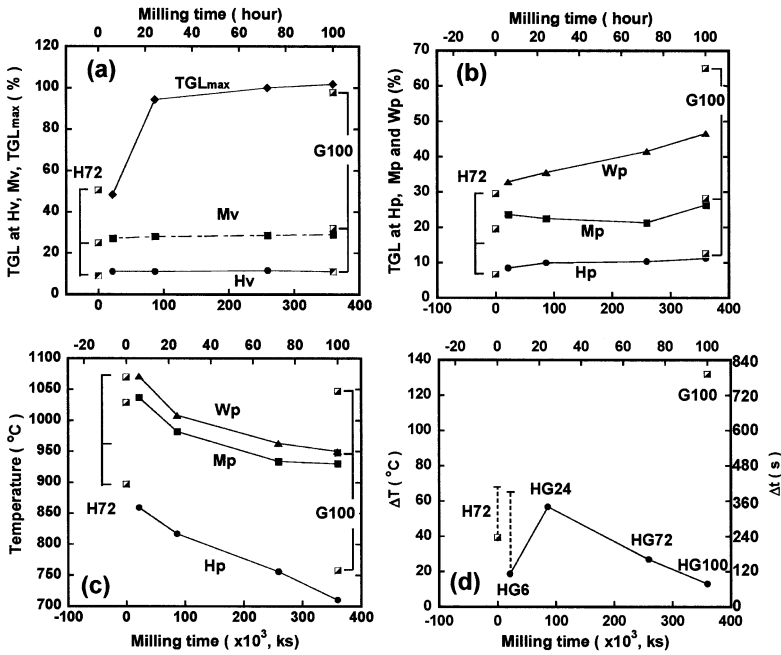
Fig. 9. Comparisons of characteristic points among different experiments.

Fig. 10. Comparison of curves of wustite–metallic iron (WF) reduction among different samples.

fects on the reduction reaction ((i) lower starting temperature of the reaction and (ii) higher rate of reaction). These effects were almost the same on the other two curves (MW and WF reduction: the details will be shown in the next section). As shown in APPENDIX, both the particles (hematite (H72) or graphite (G100)) became fine during the milling, but the final particle size and its distribution might be different between H72 and G100, which meant the different contact area. Hence, it should be noted that not only the effect of carbon reactivity but also the difference of contact area could affect the result that the degree of reduction in G100 was higher than that of H72. Since these experiments (H72 and G100) were carried out for the comparison with the milling of mixture (HG6, HG24, HG72 and HG100), it should be emphasized that the effects of milling on the mixture (temperatures at peaks (Fig. 9(c)) and ΔT (Fig. 9(d))) was more prominent. Moreover, not only the simple geometric contact area but also the distance between the oxygen in the oxide and carbon would be very important factor to understand the result of milling. These effects were more significant for the MW reduction and WF reduction as shown in the following section

3.2. Features of Curves: MW Reduction and WF Reduction

The convex curves of MW reduction and WF reduction are always overlapped as shown in Figs. 3 to 8 and also it can be understood from the values of TGL at Mv (<30.0%, Table 2). It could be noted that the reaction could be classified into the consecutive reaction. The temperatures at Mp and Wp decreased with increasing milling time, which has the same tendency as the one at Hp (Fig. 9(c)). The TGLs at Mp and Wp increased with increasing milling time as shown in Fig. 9(b), especially the one at Wp significantly increased from 32.8% in HG6 to 46.6% at HG100. Furthermore, the value of RTG at Wp extremely increased with the milling time, although the ones at Hp and Mp were almost the same (Table 2). Comparing with the result that
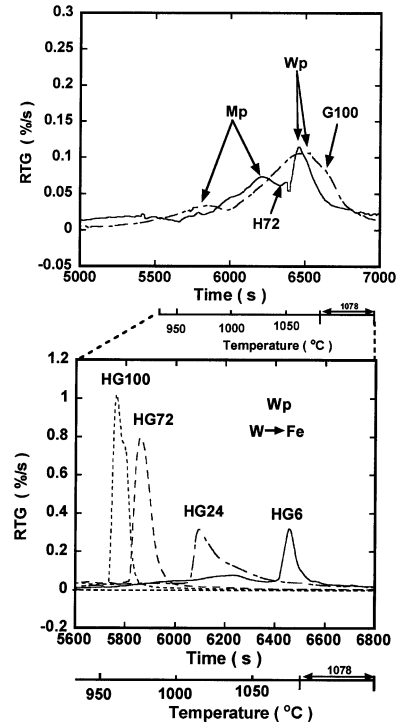
the curves of HM reduction and MW reduction were just moved toward the low temperature range, WF reduction was moved toward the low temperature range together with the increase of reaction rate (RTG).

It could be emphasized that the most notable and important factor was the ΔT (or Δt; $\Delta T = 10/60 \cdot \Delta t$ in order to constant heating up rate until 1 100°C), the width of WF reduction (Fig. 9(d)), which could be an index that the reaction finished within ΔT. In the case of H72 and HG6, the reaction degrees at the end of experiment (TGL$_{max}$) were almost 50%, so that the ΔT was relatively small because of low reaction degree, however, it could be expected that the ΔT of H72 and HG6 were quite large and might be more than the value of G100, if the TGL$_{max}$ of H72 and HG6 were reached to 100%.

Figure 10 shows the reduction curve corresponding to WF reduction in the respective experiments. It could be seen that the curves from HG6 to HG100 were changed to the small ΔT (or Δt) and moved toward the low temperature range. The shape can be called the 'pulse-like' curve which means the extremely high rate reduction, especially in HG100. In upper part of Fig. 10, the curves corresponding to WF reduction for H72 and G100 are shown, although the MW reduction curves are included. Particularly in H72, the peak of MW reduction was close to the one of WF reduction. As mentioned above, the final reaction degree was 50.57% in H72 and the area of the curve should be smallest. On the other hand, in G100, the final reaction degree was close to 100% and reduction curves between MW reduction and WF reduction relatively separated. The broad curve of WF reduction in G100 located in the same region as the MW and WF reductions in H72.

N. J. Welham and J. S. Williams showed in their work that the reactivity of graphite was considerably increased when it was subjected to ball milling. And after 100 hr

milling, graphite showed similar combustion characteristics to activated carbon.[13]

E. Kasai *et al.*[8] have carried out similar experiment using various oxide (reagent hematite and iron ores) and carbon (graphite and cokes). They reported the rapid reaction rate also in the case of the ball milling of hematite and graphite mixture. They used a planetary ball milling with seven agate balls of 15 mm diameter. Their maximum milling time was only 60 min, however, the rotation speed was 1 350 rpm, while in present study, the rotation speed was 200 rpm and the milling time was 100 hr in maximum. Although the crushing condition between the present study and Kasai *et al.* can not be compared easily, it can be said that the high crushing energy decrease the time for milling to obtain the same reaction rate. It is interesting how the respective reduction curves (HM, MW and WF reductions) were changed by the method of crushing or the difference of crushing energy.
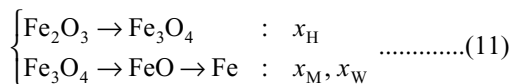
Moreover, they observed the temperature decrease at the WF reduction stage because of the large endothermic reaction. The sample weight used by Kasai *et al.* was 30 mg, while 20 mg in present study and we observed the small temperature decrease only in HG100 (Fig. 1(b)). Because of the small temperature decrease in this study, the peak of WF reduction showed the inflection point (Fig. 2(b)). It is considered that the plot of RTG made the phenomena more clear and perspicuity.

3.3. Kinetic Analysis

From the detailed observation above mentioned, it was found that the reaction in the present system was the consecutive reaction from hematite to metallic iron, exactly.

$$Fe_2O_3 \rightarrow Fe_3O_4 \rightarrow FeO \rightarrow Fe \quad ....(10)$$
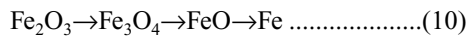
However, actually the HM reduction was separated from other reactions and MW and WF reductions were overlapped. These reactions could be taken as the single and consecutive reaction .

$$\begin{cases} Fe_2O_3 \rightarrow Fe_3O_4 & : \quad x_H \\ Fe_3O_4 \rightarrow FeO \rightarrow Fe & : \quad x_M, x_W \end{cases} \quad ....(11)$$

Hence, the kinetic analysis was carried out with the following equations.

$$RTG_H = -\frac{dx_H}{dt} = S_H k_H x_H = k'_H x_H \quad ....(12)$$

$$RTG_M = -\frac{dx_M}{dt} = S_M k_M x_M = k'_M x_M \quad ....(13)$$

$$RTG_W = -\frac{dx_W}{dt} = S_W k_W x_W - \left(-\frac{dx_M}{dt}\right) = k'_W x_W - k'_M x_M$$
$$.......................................(14)$$

where x (−) means the fraction of unreacted part of respective reactions which expressed by Reactions (7), (8) and (9) and subscripts 'H', 'M' and 'W' mean the HM, MW and WF reductions, respectively. S (−) means the specific contact area between oxide and carbon ($S = S_p/S_0$, S_p; contacting area of the particles (cm^2), S_0; total surface area of non-milling sample (cm^2)) and k (1/s) is the reaction rate con-

stant expressed by the Arrhenius equation, Eq. (15).

$$k_Y = A_Y \exp\left(\frac{-E_Y}{RT}\right), \quad (Y = H, M \text{ and } W) \quad ....(15)$$

Where A_Y (1/s) means a frequency factor, E_Y (cal/mol) means an activation energy, R (cal/mol K) is the gas constant and T (K) is the absolute temperature. Since it was difficult to know the exact values of contact area S between oxide and carbon, k' (1/s) was introduced and Eq. (16) was used for the present analysis instead of Eq. (15).

$$k'_Y = S_Y A_Y \exp\left(\frac{-E_Y}{RT}\right) = A'_Y \exp\left(\frac{-E_Y}{RT}\right),$$
$$(Y = H, M \text{ and } W) ....(16)$$

The parameter fitting to determine A_Y and E_Y was carried out and RTG curves were recalculated. The calculation result for HG100 is shown in **Fig. 11** and the obtained the rate constants for each experiments were as follows and shown in **Fig. 12**.

$$k'_H = 1 \times 10^5 \exp(-20\,000/T)$$
$$k'_M = 7 \times 10^{11} \exp(-43\,000/T) \quad \text{for HG6} .... (17a, b, c)$$
$$k'_W = 1 \times 10^{30} \exp(-100\,000/T)$$

$$k'_H = 200 \exp(-12\,000/T)$$
$$k'_M = 5 \times 10^7 \exp(-30\,000/T) \quad \text{for HG24} ....(18a, b, c)$$
$$k'_W = 1 \times 10^{32} \exp(-100\,000/T)$$

$$k'_H = 500 \exp(-12\,500/T)$$
$$k'_M = 9 \times 10^8 \exp(-32\,000/T) \quad \text{for HG72} ....(19a, b, c)$$
$$k'_W = 6 \times 10^{137} \exp(-400\,000/T)$$

$$k'_H = 10\,000 \exp(-14\,800/T)$$
$$k'_M = 9.8 \times 10^8 \exp(-32\,000/T) \quad \text{for HG100} ...(20a, b, c)$$
$$k'_W = 2.5 \times 10^{157} \exp(-450\,000/T)$$

In Fig. 11(a), the pulse-like WF reduction curve is compared between the calculation and observation. It was found that Eqs. (13) and (14) derived from the analysis of consecutive reaction were adequate to the WF reduction in the present system. In Fig. 11(c), the HM and MW reduction curves are also shown. A little overlap between HM and MW reduction was found, as the extent was very small, the single reaction analysis was not affect the result. The reduction degrees (−TGL) for HM, MW and WF reductions and total one which directly corresponds to the observed data are shown in Fig. 11(b). It should be noted that the WF reduction increases with a right angle because of extremely rapid reaction rate. The calculated line of TGL was obtained from Eq. (21).

$$TGL_{Total} = 0.1111 \times TGL_H + 0.2222 \times TGL_M$$
$$+ 0.6667 \times TGL_W.............................(21)$$

The excellent agreement between the calculation and the observation was obtained also in other experiments except the HG6 because the final reaction degree of HG6 was about 48%, since the calculation results are always 100%. In the case of short milling time, the contact area between
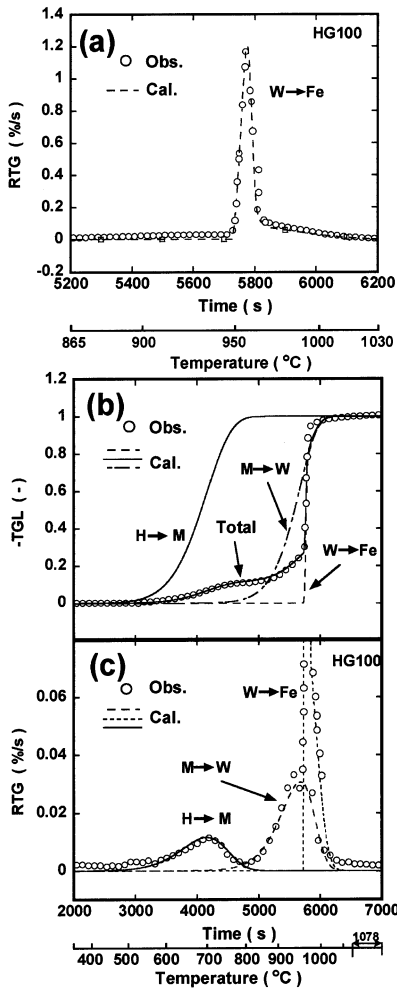
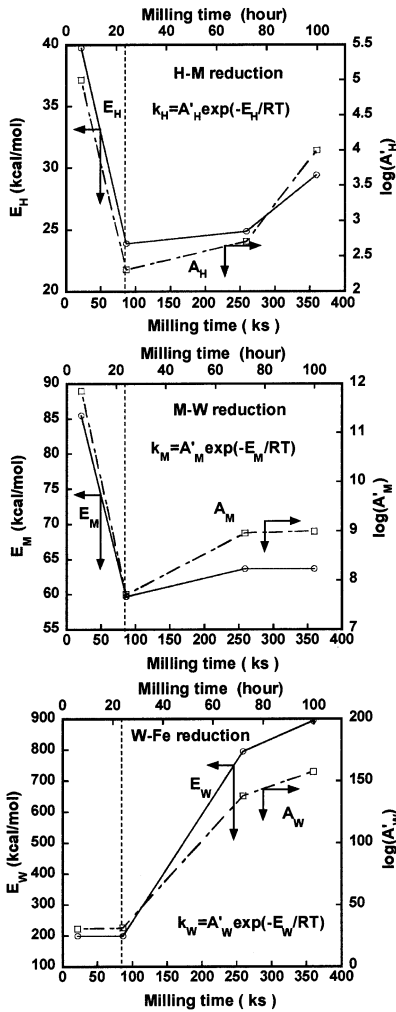**Fig. 11.** Calculation results of TGL and RTG curves in HG100 and comparison with the observation.

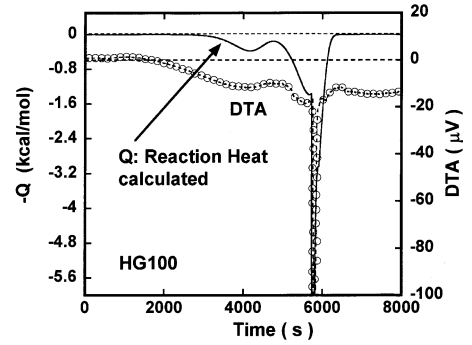**Fig. 12.** Parameters of rate constant in three reaction equations for different samples.

Fig. 13. Comparison between the reaction heat calculated and the result of DTA.

oxide and carbon will be small and the contact itself will be separated after some extent of reaction. It would be the reason of the low final reaction degree.

The obtained parameters (A'_Y and E_Y) were compared in **Fig. 12** among different milling times. As the final reaction degree was not 100% in low milling time (HG6), the variation of parameters with the milling time show the different tendency at 86 ks (24 hr). From the 86 ks, both of A'_Y and E_Y increased with increasing milling time. As mentioned in the section of introduction, these results can not understand with the simple contact area. The state of contact, which might the distance between the carbon atom and the oxygen atom in the oxide, would be important to explain the present result. The activation energy of WF reduction, E_W was 900 kcal/mol which was remarkably high value in comparison with the general chemical reaction. Although the exact explanation would be the future work, the results might be related the increase of surface energy.[14]

The change of enthalpy of each reaction of oxides with both the solid carbon and the CO gas are compared in Fig. A5 (Appendix). It can be seen that the reduction of iron oxides with solid carbon are endothermic and the values are quite high. Using these values and calculated reaction curves (HM, MW and WF), reaction heats ($-Q$: the sign was inversed for the comparison) were calculated and

shown in **Fig. 13**. It should be noted that the data from DTA is never corresponding to the reaction heat directly according the delay of heat transfer and ununiform heat flow from the electric furnace when the reaction occurred. However, the calculation result was in good agreement with the DTA data qualitatively. The DTA result shows that the data meant the endothermic reaction for the three reactions (HM, MW and WF reductions) and the calculated reaction heat ($-Q$) was always negative and mostly agreed with the observation, qualitatively. Although the base line of DTA was corrected with empty crucible, it was not perfect which was common for DTA experiment. If further correction for the base line from 2 000 to 6 500 s was conducted, more adequate DTA curve would be obtained, and qualitatively similar DTA curve to the calculation curve might be obtained. In this section, it could be concluded that the reaction expressed by Eq. (1) was the main reaction in present study and a little reaction with evolved gas occurred. Furthermore, in the case of HG6, there was a possibility of gas–solid reaction from the result of low reaction degree. However, the tendency between the calculated curve of reaction heat and the observed DTA curve was the same as HG100, which meant that the only endothermic reaction occurred throughout the experiment. It could be said that the low reaction degree of HG6 might be caused by the low

contact area (also weak contact between hematite and carbon).

4. Conclusions

The effect of ball milling of raw materials on the reduction behavior of mixture between hematite and graphite was studied. The sample mixture was treated using a planetary ball mill. The rotation speed was relatively low (200 rpm) and the milling time was continued to 100 hr to make clear the process of the milling. Heating up reduction experiments were carried out in an Ar atmosphere using TG-DTA. The mixture, containing 19.84 wt% graphite, was heated from room temperature up to about 1100°C with a constant heating rate of 10°C/min and kept at this temperature for 30 min. The obtained results could be summarized as follows:

On the Milling of Non-mixed Sample (H72 and G100):

(1) The milling was more effective on the graphite than the hematite and an active carbon resulted from longer milling time enhanced the reduction reactions of iron oxides.

On the Mixture (HG6, HG24, HG72 and HG100):

(2) The overall reaction curve consisted of three reaction curves that corresponded to the hematite–magnetite (HM), magnetite–wustite (MW) and wustite–metallic (WF) reductions. The curve of HM reduction located in low temperature range and was separated from other two curves. MW and WF reduction curves overlapped.

(3) The peaks of each reaction curves moved toward the low temperature range and the reaction degree increased with increasing milling time.

(4) The WF reduction curve exhibited the pulse-like shape which meant extremely rapid reaction rate and the temperature difference which corresponded the width of pulse decreased with the milling time.

(5) Kinetic analysis applying the single and consecutive reactions was carried out and the rate constants were obtained by fitting the each curves to the observed one. The calculated curve was in good agreement with the observation.

(6) The variations of parameters on the rate constant increased with the milling time, except the low milling time (less than 24 hr).

(7) The calculation result of reaction heat showed the same tendency as the DTA result, which meant the endothermic reaction of oxide and solid carbon.

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Appendix

(a) Variation of Particle Size and Crystalline Size During the Milling

We carried out the XRD analysis, SEM and TEM observation of the particle obtained by the milling. As the phenomena were not simple, the results about the details of those analyses will be published in near future. However, it would be important to know the state of particle after milling for understanding the result of TG-DTA. In present paper, some of results were shown as follows:

Figure A1 shows the results of SEM observation of hematite particle before and after the milling ((a): reagent hematite particles, (b): 26 hr milling). The original particle size is 1 to 9 μm in SEM observation, however, the crystalline size might be around 0.1 μm (100 nm). The crystalline size in the hematite particle was about 80 nm, which was examined by XRD and evaluated by Scherrer's equation (**Fig. A2**). After 26 hr milling, the particle size decreased from 0.1 to 0.5 μm. However, as the limit of SEM observation for small particle was about 0.1 μm, the smaller particle than 0.1 μm would exist in the sample, which could be confirmed by XRD. It was considered that the hematite sample used for G100 consisted of the particle shown in Fig. A1(a) and the one for H72 was shown in Fig. A1(b).

It should be noted that the particle size and crystalline size was different especially in shorter milling time, however, with increase of milling time, the particle size was close to the crystalline size. Figure A2 shows the variations of hematite crystalline size both in the mixture (hematite and graphite) and the hematite only, which were calculated by Scherrer's equation using the peaks of XRD ((300)$_H$, (110)$_H$ and (104)$_H$). The crystalline size in the single hematite sample decreased with increasing milling time. On the other hand, the crystalline size of hematite in the mixture increased from the beginning of milling and showed almost constant value. Moreover, the particular plane (300) increased larger than the other planes ((110), (104)), which might show the reoxidation of iron oxide. The gas analysis was carried out using the atmosphere-controlled vial (Ar atmosphere) and the CO gas evolution was confirmed, which meant that the reduction reaction between the hematite and the solid carbon occurred during the milling. Furthermore, the crystalline size of hematite in the mixture under Ar atmosphere decreased with increasing milling time.

On the other hand, the crystalline size of graphite decreased with increasing milling time both in the single graphite sample and the mixture without any relationship with atmosphere (**Fig. A3**, which is the result from Air atmosphere).

From these results, it could be considered that the reduction and reoxidation of hematite were repeated during the

Fig. A1. SEM observation of reagent hematite particle.
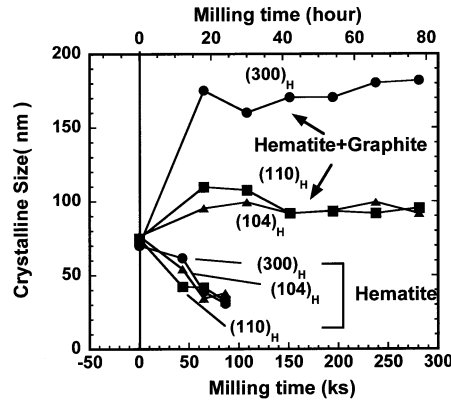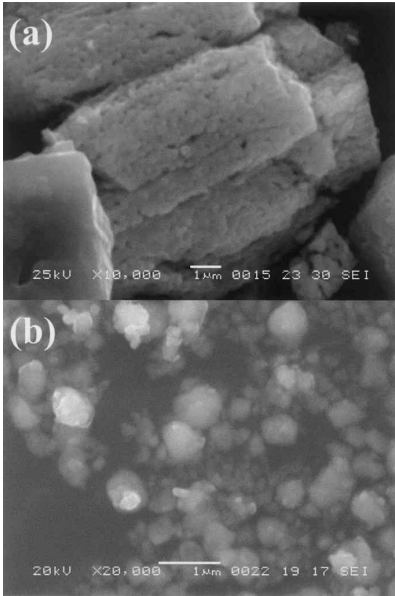(a) before milling (b) after 26 hr milling.

Fig. A2. Variations of crystalline size of hematite with milling time (in the mixture and the single hematite).

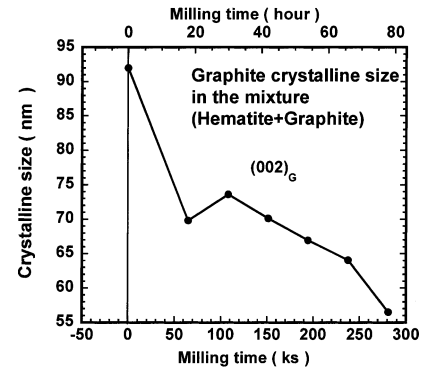Fig. A3. Variations of crystalline size of graphite in the mixture with milling time.
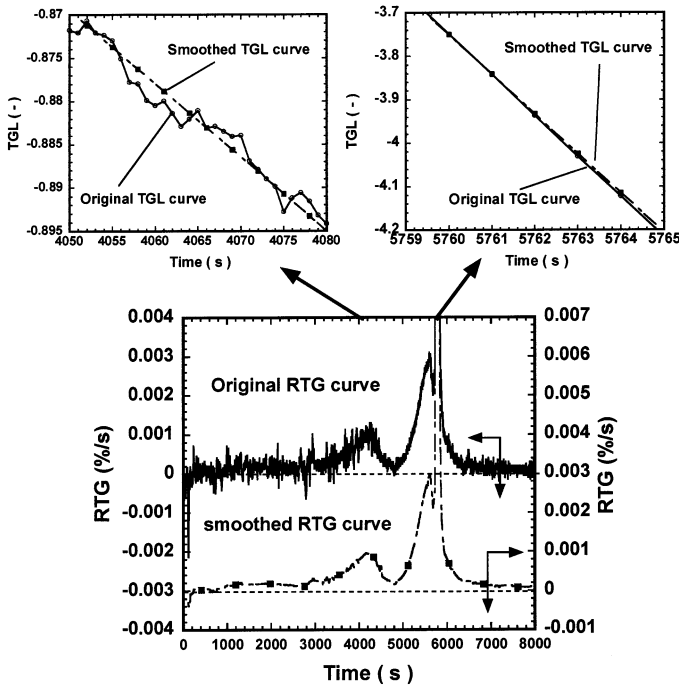

Fig. A4. Smoothing procedure for getting the curve of reaction rate (RTG) from the discrete data of weight loss curve (TGL).
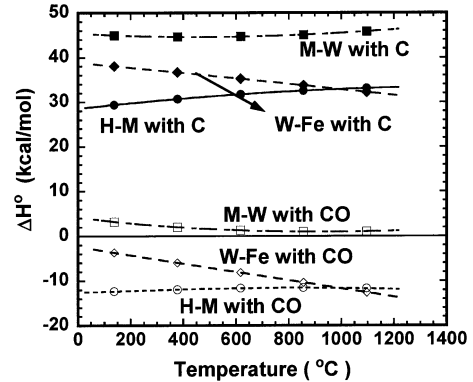

Fig. A5. Change of enthalpy of each reaction.

milling in Air atmosphere. The results could be summarized as follows:

(1) the graphite crystalline decreased with the milling as shown in Fig. A3.

(2) the hematite crystalline was almost constant and about 100 to 170 nm as shown in Fig. A2 (in Air atmosphere).

(3) the hematite particle for H72 was about 40 nm and the particle morphology was shown in Fig. A1(b).

(4) the hematite particle size for G100 was about 1 to 9 μm (Fig. A1(a)).

(b) Smoothing Method of RTG Curve

In the case of TG measurement, most of discussions have been carried out using the weight loss curve, which meant the reaction degree (TGL curve). The rate of reaction has been rarely used for discussion, because the numerical differentiation for the discrete data was relatively difficult and the scattering increased. However, when we could get the curve of reaction rate (RTG) adequately, several phenomena could be separated more effectively. It was important to select the adequate Δt for the differentiation at a given region. In this study, the longer region (100 to 500 s) was selected for HM and MW reduction (relatively slower reaction) and the shorter region (1 to 5 s) was selected for WF reduction (rapid reaction). **Figure A4** show the one example of smoothing of TGL curve for getting smooth RTG curve.

(c) Figure A5 Shows the Variation of Enthalpy Change of Each Reaction.

Reference: JANAF Thermochemical Tables, 3rd ed., J. Physi. Chem. Ref. Data, (1985).