

REDUCTION OF POWDERY FERRIC OXIDE MIXED WITH GRAPHITE PARTICLES*

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The reactions of powdery ferric oxide mixed with graphite particles in the stream of nitrogen were carried out at 1050~1150°C. The overall reduction process of ferric oxide to metallic iron proceeded through two stages.

In the first stage, ferric oxide was reduced to magnetite and then to ferrous oxide by carbon monoxide, yielding carbon dioxide. Carbon monoxide is produced by reaction between graphite and carbon dioxide (carbon solution reaction), which seems to control the rate of overall reaction.

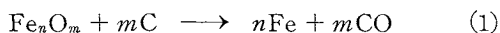
In the second stage occur the reduction of ferrous oxide to iron and the carbon solution reaction. This stage of the reaction can be assumed to proceed autocatalytically and is greatly influenced by the size of ferric oxide and addition of bentonite.

Effects of the particle size, addition of bentonite and contact condition of particles on the rate of overall reduction are discussed.

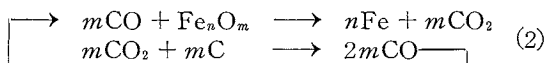
Introduction

At elevated temperature above 900°C either in vacuum or inert gas atmosphere, the mixture of powdery iron oxide and solid carbon generates carbon monoxide and carbon dioxide to give metallic iron. In order to explain the above phenomena, the following two mechanisms have been applied so far⁽¹⁾.

1. "Direct Reduction" in which direct interaction of solids occurs.



2. "Indirect reduction" in which carbon monoxide as reductant is consumed and regenerated by solids.



Many investigations have been reported about the above reaction system, mostly associated with the effort to account for the mechanism of reduction in the blastfurnace process^(7,9). Since the main interest of those investigations has been concerned with the rate and mechanism of the reaction (1), most investigations^(1,3,15) have been performed under high vacuum condition to eliminate the effect of carbon monoxide formed through carbon solution reaction. In inert gas atmosphere, the view most widely accepted at present is that the two stage mechanism (2) is the more probable^(2,6,11). Gavrilova⁽⁵⁾ and Rostovtsev⁽¹⁰⁾ reported gas-solid interaction on the basis of the above mechanism.

The burden materials of blast furnaces are currently receiving considerable attention and the use of both sinter and pellets has led to big productivity gains. During the sintering and pelletizing process it is

customary to add solid fuel to the mixtures to provide the necessary heat for agglomeration. The prospect of achieving considerable reduction during agglomeration under suitable conditions is arousing much interest. Thus, it is of some significance to treat this reaction system in a different way from the above investigations.

To throw light upon the above subject, powdery iron oxide well mixed with fine carbon particles was heated under inert atmosphere, and the effects of temperature, composition and dimension of the raw materials upon the overall reaction rate were studied.

Experimental Apparatus

The Experimental apparatus is shown in **Fig. 1**. Nitrogen gas was sent into the lower part of a silica tube (22mm I.D.) placed at the center of an electric furnace. A silica bucket (20mm height, 16mm I.D.) containing the test sample was suspended by a platinum chain at the middle of the heated silica tube. At the upper part of the silica tube, there was an opening for gas sampling. Weight change was measured by observing the displacement of the silica balance by cathetometer.

Test Samples

The materials were chosen as pure as possible. Ferric oxide (99% Fe₂O₃) was prepared by roasting of iron nitrate at 800°C. Porous ferric oxide particles thus prepared with specific gravity 4.7 were sieved to various sizes, namely 325, 270, 250, 200, 150 and 100 meshes. Electrode graphite (99.8% C, specific weight 2.2, 31% of pore volume) was crushed and sieved to 325, 250, 200, 150, 100, 80 and 65 meshes. Nominal particle sizes were given by mean root squares of

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openings of two mesh sizes. Only particles passing 325 mesh are called fine particles in this paper. Fine particles of Fe_2O_3 had mean size of 20μ measured by precipitation method. 66% fine graphite particles in weight were smaller than 5μ . Fine bentonite (SiO_2 77.3%, Al_2O_3 13.5%) smaller than 300 mesh was added to the sample in some specific runs. Standard test sample of mixture contained 0.8gr of Fe_2O_3 and 0.2gr of graphite without bentonite. It was carefully mixed and packed in silica bucket without any binder (void fraction 0.8).

Procedure

The silica bucket suspended by Pt chain and silica spring was inserted into the silica tube heated at constant temperature. Measurement of reaction time and weight change was commenced at the instant of insertion. Gaseous products from the bucket were continuously removed by the nitrogen stream at constant flow rate (200cc at room temperature/min). Gas samples were taken into sampling devices at suitable time intervals and were analysed by gas-chromatograph to give the composition of the gaseous products. Overall reaction rate was calculated from the flow rate of gas produced from the reacting solids. Experimental data of decreasing weight measured by balance were employed only to check the experimental errors involved in gas analysis and in the time lag originated in the sampling of gas.

Experimental Results

Fig. 2 shows the feature of the reaction in the mixture of fine ferric oxide with fine powdery graphite in the temperature range of 1050 – 1150°C . As clearly shown in those figures, the reduction process was found to proceed by two steps. **Fig. 2-3** and **2-4** indicate that the first step was up to about 30% reduction degree. (When Fe_2O_3 was reduced to 2FeO , reduction degree was 33%.) Nearly all the generating gas in the first step was carbon dioxide as illustrated in **Fig. 2-2**. If the total amount of ferric oxide was reduced to ferrous oxide (FeO) and produced carbon dioxide, the weight of the sample mixture decreased to 89% compared to the initial weight. **Fig. 2-1** shows that the rate of weight decrease changed when the weight of the test sample decreased to 89–90% of the initial weight. Therefore, it may be concluded that nearly all Fe_2O_3 in the reaction system was reduced to FeO and then metallic iron was formed from FeO . The above postulate was confirmed by the result of chemical analysis of the sample. A sample at a reaction time of 2.5 minutes at 1100°C was analysed to find a mixture of FeO and graphite with a trace of metallic iron. As shown in **Fig. 2-5**, the content of carbon monoxide in the generating gas increased rapidly up to about 80% from a small value at the initial stage of reduction. The most remarkable feature was that the reduction rate had an abrupt change at the

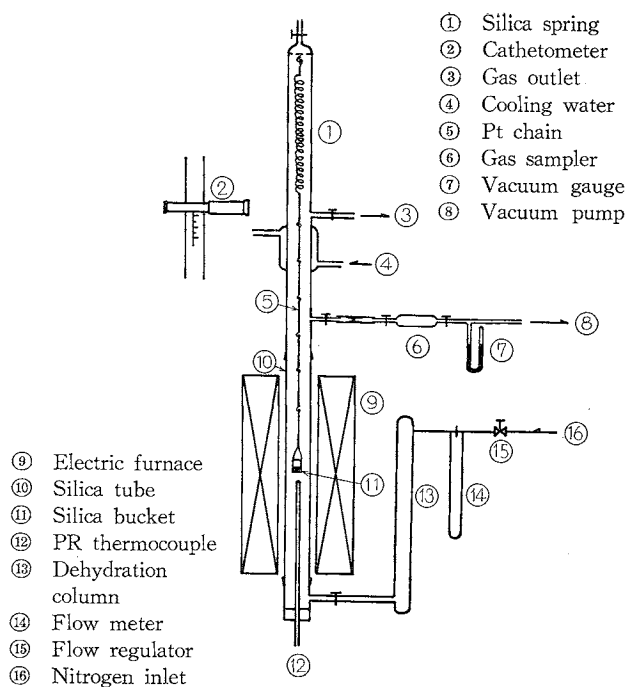


Fig. 1 Experimental apparatus

reduction degree of about 33%.

As shown in **Fig. 3**, the rate of reduction became large when the weight ratio of carbon to Fe_2O_3 in the sample mixture was increased.

In several runs bentonite was added to the mixture of iron oxide and graphite without any binder, and some results were shown in **Fig. 4**. The effect of bentonite became marked during the second step of the reduction, and the reduction rate became slower for larger quantities of bentonite under the above experimental conditions. In the above case CO content in the produced gas was scarcely changed by the addition of bentonite. When the samples were pressed by the pressure of $770\text{Kg}/\text{cm}^2$, the porosities became about 0.4 from the initial value of 0.8. The above treatment gave a much larger rate of reaction than ordinary samples without bentonite, but gave a smaller rate when bentonite was added into the mixture as in **Fig. 5**. The solid-phase reaction products, composed of Fe , FeO and excess C, were reduced in size and porosity, and the initial mixture of powders became a granule with each powder sintering together.

Fig. 6 is for the case when the size of the graphite particles was varied while Fe_2O_3 particles were kept fine. Existence of two steps for the reduction reactions can be found more clearly, and the rate of both steps became slower for coarser graphite particles.

The effects of changing size of Fe_2O_3 particles are illustrated in **Fig. 7**, when graphite particles were kept fine. The rate of the first step was found to be independent of the particle size of Fe_2O_3 , whereas the rate of the second step was greatly diminished with the increasing size of Fe_2O_3 particles.

Fig. 8 shows the results obtained in the reaction for a mixture of coarse Fe_2O_3 and graphite. Compared

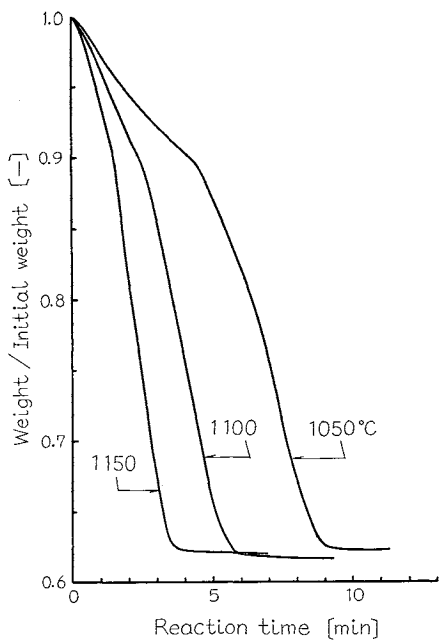


Fig. 2-1 Weight change of the sample mixture

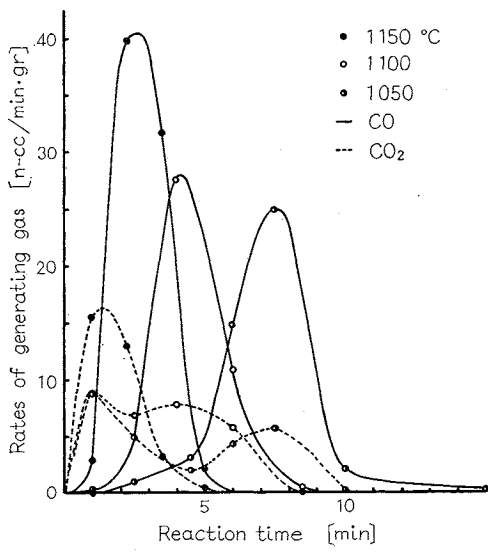


Fig. 2-2 Rates of generating gas

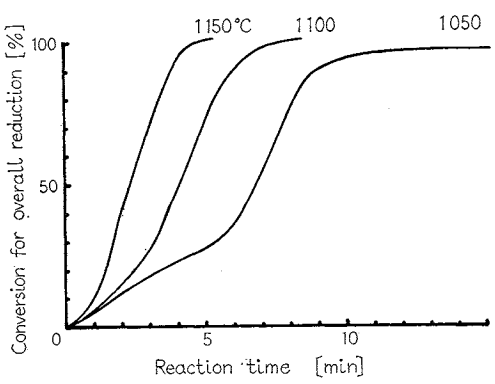


Fig. 2-3 Reduction degree curves

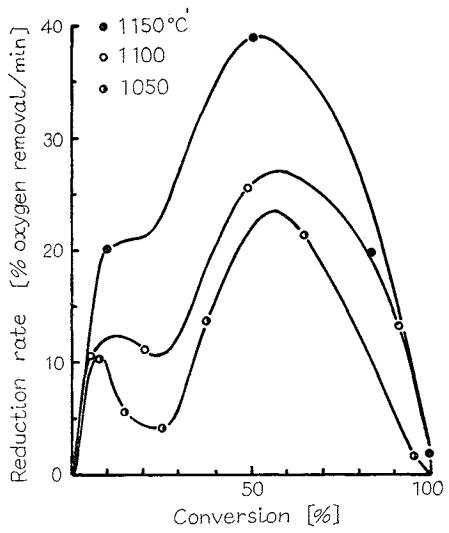


Fig. 2-4 Reduction rate versus conversion

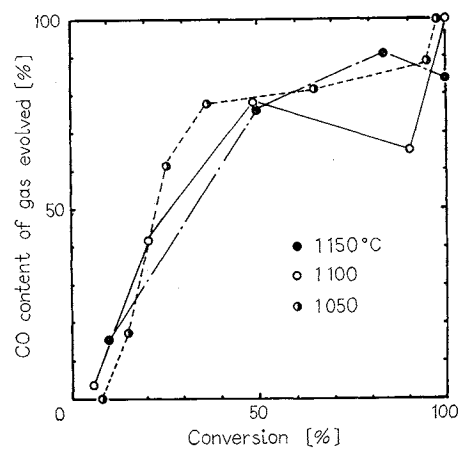


Fig. 2-5 Change of gas compositions

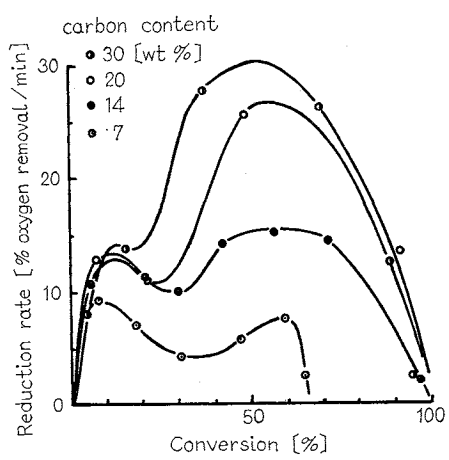


Fig. 3 Effect of carbon content on the reduction rate (1100 °C, fine particles)

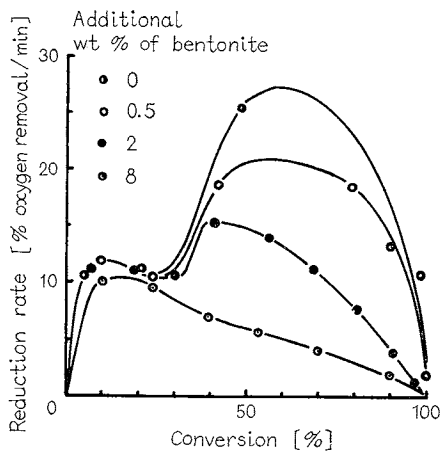


Fig. 4 Effect of addition of bentonite on the reduction rate (1100°C, fine particles)

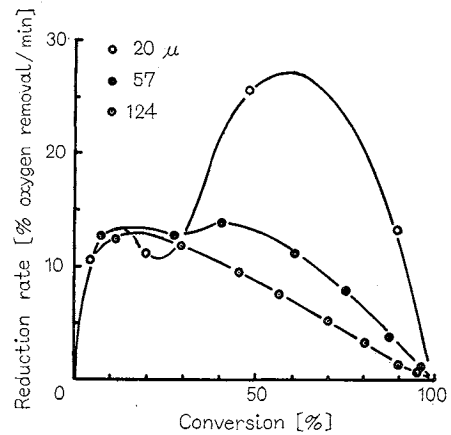


Fig. 7 Dependence of particle sizes of Fe_2O_3 on the reduction rates at 1100°C (fine carbon)

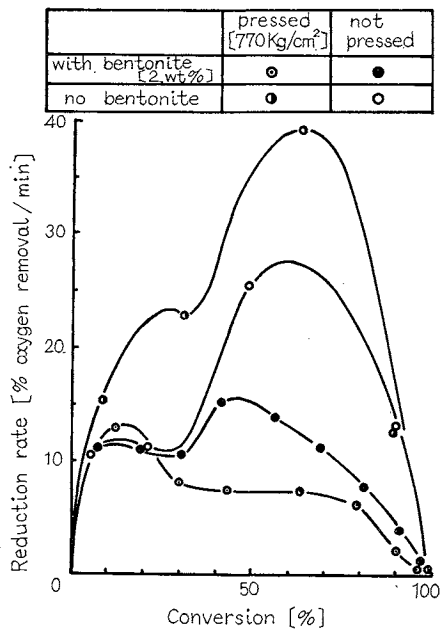


Fig. 5 Reduction rate versus conversion when the sample mixtures were pressed (1100°C, fine particles)

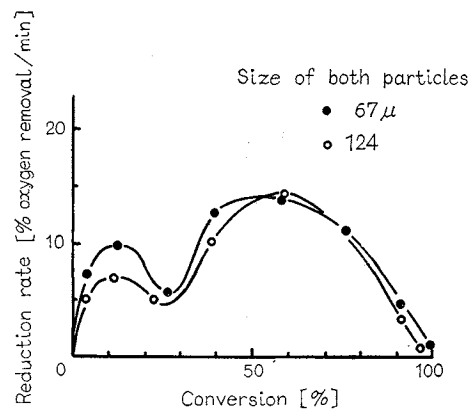


Fig. 8 Reduction rate versus conversion when both carbon and Fe_2O_3 particles are coarse, at 1100°C

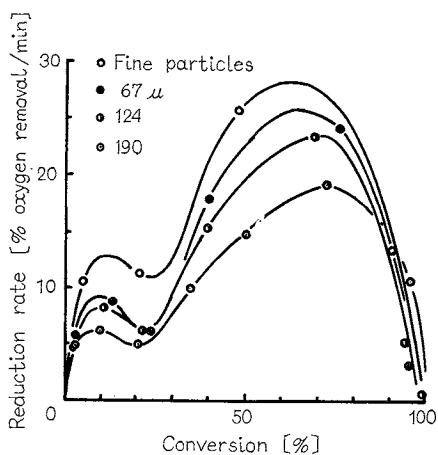
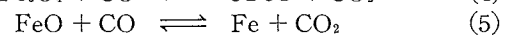
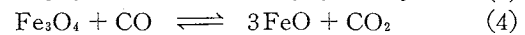
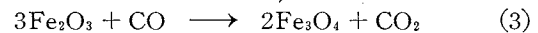


Fig. 6 Dependence of particle sizes of carbon on the reduction rate at 1100°C (fine Fe_2O_3)

with Fig. 7, it may be noted that the reduction rate of the second step of coarse Fe_2O_3 was smaller for the mixture with the fine graphite particles than with the coarse ones.

Discussion of the Results

According to the experimental results in the present work as well as those previously reported^{2,5,10,11}, reaction mechanisms represented by Eq. (2) seems to occur under the present experimental conditions. A molecule of CO formed in the heated bed of the reaction mixture reduces the iron oxide to give CO_2 . It reacts with carbon to produce two molecules of CO, which are available for further reduction. In detail we can write as follows;



Furthermore, the experimental results in the present work indicate that reaction (5) occurs in this reaction system just after nearly all Fe_2O_3 is reduced to FeO by the reactions (3) and (4). The activation energies calculated from overall reduction rates at two levels

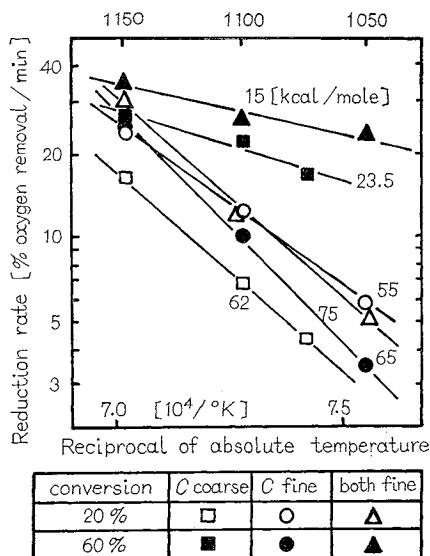


Fig. 9 Activation energies measured

of reduction degree, 20% and 60%, are shown in Fig. 9. The values of the activation energies are classified into two ranges: 15, 23.5 kcal/mole at the second stage of the reduction when Fe_2O_3 is fine; and 55, 62, 65 and 75 kcal/mol in other cases. The reported activation energies for reduction of FeO by CO (4) range from 15 to 30 kcal/mole^{8,12)} and for the carbon solution reaction (5) from 60 to 80 kcal/mole^{13,14)}.

The first stage of the reduction, having activation energies of 55, 62 and 65 kcal/mole, shows that the rate is not affected by the size of Fe_2O_3 and that produced gas is almost exclusively composed of CO_2 . It is likely, therefore, that in the early stage of reduction the rate of carbon solution is controlling in the overall process. This is in agreement with the results of other investigations^{2,5,6,10,11)}.

During the first stage, as soon as CO is produced by the carbon solution reaction, it reacts with iron oxide to give CO_2 , because the carbon solution reaction is controlling in the overall process. The overall reaction rate is not remarkably accelerated even if the reduction rate of FeO is much faster than that of Fe_2O_3 and Fe_3O_4 , which is not likely to occur. Therefore, such fast reaction rate of the second stage compared with that of the first stage cannot be attained except where the carbon solution reaction is accelerated for some reason or other. Furthermore, the second stage has the characteristics of a self-catalysed process having the maximum rate of reaction, as our experimental results indicate. This acceleration of carbon solution may be interpreted by the catalytic effect of metallic iron produced on the surface of the carbon¹⁰⁾. This might be supported by the fact that the reactions of the fine Fe_2O_3 particles which seem to have better contact with carbon give a faster rate of reduction than those of the coarse ones.

It may not be concluded, however, that the second stage of the reaction of fine Fe_2O_3 particles is controlled by the reduction of FeO (5). Firstly because the composition of produced gas was close to that of equilibrium concentration of reaction (5) (74~76% at 1050~1150°C), and secondly because even the reaction of coarse Fe_2O_3 particles is controlled by the carbon solution reaction.

The addition of bentonite and pressing of sample mixture influenced appreciably the rate of the second stage, indicating an effect on the interaction between metallic iron and carbon.

This reaction seems to be initiated by the oxygen adsorbed on the surface of the samples or remaining inside the silica bucket, otherwise by CO or CO_2 produced by solid-solid reaction at the points of contact of Fe_2O_3 and carbon.

Conclusion

The reactions of powdery ferric oxide mixed with graphite particles were carried out in a stream of nitrogen at 1050~1150°C.

1. Gas solid reactions as shown in Eqs. (3), (4), (5) and (6) are proposed to interpret the overall reduction process in the above mixture.
2. The first stage of the reactions (3), (4) and (6) seems to be controlled by carbon solution (6).
3. The second stage of the reactions (5) and (6) can be assumed to proceed autocatalytically and is greatly influenced by the size of Fe_2O_3 and addition of bentonite.

Effects of the particle size, addition of bentonite and contact condition of particles on the overall rate of reduction process were discussed.

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