Microwave Induced Solid–Solid Reactions between Fe₃O₄ and Carbon Black Powders

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The reduction of 1 µm diameter magnetite by 22 µm diameter carbon black in powder mixture under a constant microwave power of 2.8 kW at 2.45 GHz up to 1200°C was investigated. The initial mixture mass was 6 g in every experiment. Temperature and mass loss of the reacting mixture as a function of time were continuously recorded. The temperature measurement was from 220°C and the mass loss from the start of irradiation. Five different mixtures were irradiated; all of them up to 800°C, three up to 1000°C and two up to 1200°C. All mixtures registered measurable mass losses below 220°C. Total reduction of magnetite to wustite was accomplished below an average temperature of 651°C. Reduction rates as a function of the irradiation time were calculated. The reduction presented three distinctive stages; a initial very fast stage with an average maximum reduction rate of 0.017 g/s, a second stage of constant very low reduction rate 0.0017 g/s, and a third one with a maximum average reduction rate of 0.0045 g/s. During the first stage all the magnetite was reduced to wustite and some wustite to iron. The reduction of magnetite to wustite is shown to take place through a series of consecutive reactions involving solid–solid reactions of magnetite with carbon black as well as solid–gas reactions. Under microwave irradiation true direct reduction occurs at much lower temperatures than under conventional heating. The results can not be explained to occur by thermal effects but by the so called microwave effects.

KEY WORDS: magnetite; carbon black; microwave irradiation; solid–solid reaction; microwave effects.

1. Introduction

The effectiveness of microwave energy in the carbothermic reduction of iron oxides has been extensively demonstrated as previously summarized by the authors in a previous communication.¹ Ishizaki and Nagata² showed that microwave irradiated magnetite ore-coal composites were rapidly smelted to produce pig iron. The heating rate of the pellets was found to be independent of the mass but strongly dependent on the applied power. With a power supply of 3 kW the initial heating was extremely fast but with 1 kW it took a very long time to reach 600°C that was the minimum detectable temperature. In order to study the mechanism of the carbothermal reduction reaction of magnetite under microwave irradiation, the authors used pure magnetite and carbon black in powder mix irradiated in a different experimental system with a minimum detectable temperature of 220°C and a constant power supply of 2.8 kW.³ The results can be summarized as follows. Magnetite selectively absorbs microwave energy below approximately 650°C; meanwhile carbon black absorbs it in the whole temperature range. The reduction of magnetite to wustite was demonstrated to occur from at least a measured temperature of 400°C but XRD patterns of reaction products of different portions indicated that the reduction did not occur homogeneously. In mixtures irradiated up to 400 and 600°C most advanced portions showed the presence of wustite and small amounts of iron; meanwhile there were other portions of almost totally magnetite. On the other hand the products of the mixture heated up to 800°C showed to be alike all over the mass with only wustite and iron in similar proportions.

The present communication is an extension of the upper mentioned work attempting to obtain a better understanding of the mechanism involved in the reduction of magnetite in carbon black powder mixtures under microwave irradiation.

2. Experimental

2.1. Materials

Commercially available (Fe₂O₄) powder (Soekawa Chemical Co.; 99% purity) and a commercial 22 µm diameter carbon black powder (Koso Chemical Co.; 100%) were used as the raw materials.

Powder mixtures with 89.46 mass% of magnetite and 10.44 mass% of carbon black were prepared. The carbon percentage was determined considering that all oxygen atoms in magnetite will be converted to CO₂ gas and pig iron with 2 mass% of carbon is produced. The total mass of mixture microwave irradiated was 6 g.
2.2. Experimental Conditions

A stainless steel pentagonal shape microwave chamber suitable for vertical as well as horizontal sample irradiation chamber set ups was used. A 2.45 GHz microwave field was generated by four magnetrons; two of 600 W located at both sides and two of 800 W located in the backside of the chamber respectively. During the experiment all magnetrons were activated at their maximum potential with a resulting power of 2.8 kW. This constant microwave power was applied from the start to the end of irradiation. A schematic illustration of the microwave chamber and the distribution of magnetrons have been presented elsewhere. 3)

The atmosphere of the sample irradiation chamber was nitrogen and it was separated from air by a transparent silica tube. The experimental system was purged with nitrogen gas until the partial pressure of oxygen reached a value of \(1.0 \times 10^{-4}\) atm.

To measure the temperature of the sample, a two colors radiation thermometer (Japan Sensor Co.; FTZ2-R220S-50822) was used. The temperature measurement range of this thermometer was from 220°C to 1 700°C. The size of the temperature measurement point was about 5.0 mm diameter. This thermometer was connected to a personal computer to monitor the temperature of the sample and recorded at about 5 s intervals.

2.3. Sample Mass Loss Measurement

The mass loss of samples was followed in situ by a thermo balance (CAHN Co.; CAHN-1000) with the experimental system shown in Fig. 1. One-end-closed transparent silica tube and crucible were used to be able to measure the temperature of the sample from the side by the radiation thermometer. The tube was set vertically at the center of the chamber and nitrogen gas (99.999%) was flowed at 100 mL/min from the top to the bottom of the tube. The crucible was suspended by a transparent silica hook connected to the thermo balance to measure the weight in situ. The mass loss was monitored by the same PC of the temperature at about 5 s intervals from about 1 min before starting the MW irradiation. Inside of the transparent silica tube porous alumina isolators (Isolite Insulating Products Co.; LAP-165) were used. An alumina blanket with silicon carbide heating auxiliary was used. The sample weight was about 6.0 g. Further details have been presented elsewhere. 3)

2.4. Off-gas Composition Measurements

Samples of nitrogen purged off-gas were taken at the sampling point indicated in Fig. 1 using 2.5 mL gastight syringes (Ito Co.; MS-GAN25). The sampling intervals were as follows: from the start of MW irradiation up to 2 min, 10 s, from 2 to 6 min, 20 s and from 6 to 7 min, 30 s.

The gas samples were analyzed by gas chromatography (Shimadzu; GC-8A). The carrier gas was 99.999% helium with a flow of 30 mL/min. A Shimadzu; SHINCARBON ST 6 m×0.3 mm stainless column was used. The initial temperature was 60°C and 12 min after the injection it was increased to 200°C at a rate of 10°C/min. The injection volume was 1 mL. Calibration curve method was used to quantify the amount of each gas in the mixture. Six standard CO, CO$_2$, N$_2$ gas mixtures and the pure gases were used to obtain the calibration curve.

3. Results

3.1. Temperature Increase and Mass Loss of Mixtures

The temperature of mixtures was continuously monitored during the microwave irradiation from to 220 up to 800, 1 000 and 1 200°C. The time temperature profiles of mixtures irradiated up to different temperatures are shown in Fig. 2(a). Initially the temperature of mixtures increases rapidly up to about 650°C for most mixtures. A detailed discussion about the mechanism involved in the temperature increase of these mixtures has been presented elsewhere. 3)
radiated mixtures are shown in obtained reduction rates as a function of time for all the ir-

4. Discussion

Fig. 3. Change in off-gas composition during the carbothermal reduction of magnetite under microwave irradiation.

The mass weight of mixtures was continuously monitored from the start until the end of the microwave irradiation. The time mass weight profiles are shown in Fig. 2(b). It is observed that all mixtures registered initial fast mass loss beginning at an average time of 22 s after the start of irradiation and continued up to about 70 s. After this time there is an additional small mass loss up to about 130 s. From this point and up to about 300 s the rate of loss is very low. From 300 s up to the end the rate of loss shows another maximum.

3.2. Off-gas Composition

Analysis of the evolved gasses was performed for one of the mixtures irradiated up to 800°C. Figure 3 shows the results of the gas analysis. The time when the irradiation was stopped is indicated. Since the flow of the carrier gas (N2) was slow, the data presents a tale of CO and CO2 gases not completely purged when the irradiation was stopped. The corresponding amount of CO and CO2 gas evolved at each sampling time was calculated using the gas chromatography analysis results fractions of N2, CO and CO2 in the mixture and taking into account that the flow of N2 gas was kept constant. The time scale has been corrected in accordance with the total gas flow at each sampling. The time lag was between 10 and 30 s. The presented data does not have absolute quantitative value but it is presented to show the relative positions in time and quantities of CO and CO2 evolved gases during the carbothermal reduction of magnetite under microwave irradiation. It is observed that CO2 gas was produced in considerable amounts during the initial mass loss and that it was evolved previous to the evolution of CO gas. After reaching a first initial maximum amount the evolution of both gases decreases. The decrease of CO2 is faster than for CO and the amount of CO gas is always larger than the amount of CO2 gas.

4. Discussion

4.1. Reduction Behavior

Reduction rates were calculated from the data presented in Fig. 2(b) using subsequent averages of eleven points. The obtained reduction rates as a function of time for all the irradiated mixtures are shown in Fig. 4(a). The results show more clearly the three different stages visualized in Fig. 2(b). The starting and finishing times with the corresponding deviations are marked in the figure.

4.1.1. Stage I

Stage I is characterized by a very fast reduction rate starting at an average time of irradiation of 22 s. The rate reaches an average maximum value of 0.017 g/s at an average time of 55 s and decreases sharply afterwards reaching a minimum value of about 0.002 g/s after about 120 s of irradiation.

The reduced mass amount of mixture under the reduction rates as a function of time curves up to 130 s for all the mixtures shown in Fig. 4(a) were separated into various peaks as shown in Figs. 4(b)–4(f). It is observed that the five mixtures do not show identical amounts for any of the peaks but show similar patterns for the five microwave irradiated mixtures. This is in agreement with the previously published results about the heterogeneity of the reactions occurring inside of the microwave irradiated mass.

The area of each peak represents masses of C+O loss during different reactions. The possible reactions that can occur in a carbothermal reduction of magnetite are listed bellow.

\[
\begin{align*}
\text{Fe}_2\text{O}_4 + 2C(s) &\rightarrow 3\text{FeO}(s) + 2\text{CO}_2 \hspace{1cm} (1) \\
\text{Fe}_2\text{O}_3 + 4C(s) &\rightarrow 3\text{Fe}(s) + 4\text{CO} \hspace{1cm} (2) \\
2\text{Fe}_2\text{O}_3 + \text{C}(s) &\rightarrow 6\text{FeO} + \text{CO}_2 \hspace{1cm} (3) \\
3\text{Fe}_2\text{O}_3 + \text{C}(s) &\rightarrow 3\text{FeO} + 2\text{CO}_2 \hspace{1cm} (4) \\
2\text{FeO} + \text{C}(s) &\rightarrow 2\text{Fe}(s) + \text{CO}_2 \hspace{1cm} (5) \\
\text{FeO} + \text{C}(s) &\rightarrow \text{Fe}(s) + \text{CO} \hspace{1cm} (6) \\
\text{Fe}_2\text{O}_3 + \text{CO} &\rightarrow 3\text{FeO} + \text{CO}_2 \hspace{1cm} (7) \\
\text{FeO} + \text{CO} &\rightarrow \text{Fe} + \text{CO}_2 \hspace{1cm} (8) \\
\text{CO}_2 + \text{C}(s) &\rightarrow 2\text{CO} \hspace{1cm} (9) 
\end{align*}
\]

Reactions (1) to (4) are solid reactions between magnetite and carbon leading to iron or wustite. The XRD diffraction patterns of mixtures irradiated up to 400 and 600°C indicated that the reduction product of magnetite was primarily wustite with very small amounts of iron. The amount of iron present in the irradiated mass up to 400°C did not change by irradiating up to 600°C but increased considerably when the irradiation was applied up to 800°C. Considering the results of the generated gasses shown in Fig. 3 it is postulated that when the applied microwave irradiation is strong enough, in Stage I both magnetite and carbon being very strong microwave absorbers may absorb all the available microwaves and undergo solid–solid reactions leading primarily to wustite through reactions (3) and/or (4). At the beginning of the irradiation magnetite being present in the highest concentration may react with solid carbon through reaction (3) evolving CO2 gas and when the concentration of magnetite decreases reaction (4) evolving CO gas becomes predominant. In accordance with this reasoning, the mass reduction of peak 1 is assigned to reaction (3) and the mass reduction of peak 2 to reaction (4). The evolved CO gas may thereafter react with not yet reduced magnetite through reaction (7) and evolve CO2 gas. Therefore the reduction obtained as the area of peak 3 is assigned to reaction (7). After all the magnetite has been reduced, and still there is remaining CO gas pro-
duced by reaction (4) it may react with wustite though reaction (8). When the mixture has reached a temperature of about 600°C, the evolved CO₂ gas may react with carbon through reaction (9) to produce CO gas. According to this postulation the reduction mass of peak 4 corresponds to generation of CO gas through reaction (9). After all the magnetite has been reduced to wustite and still there is CO gas available, the reduction of wustite to iron is accomplished same as under conventional heating through reaction (8). The mass reduction under peak 5 is then assigned to occur by reaction (8).

A summary of the reactions responsible for the masses reduced under each peak are shown in Table 1.

4.1.2. Stage II

Stage II is characterized by a more or less constant rate of reduction averaging 0.0017 g/s that stays at this low level up to about 300 s. In this stage, reactions (8) and (9) continue alternating at an almost constant low rate. Possible explanations for the low rate of reduction are the fact that wustite is not a good microwave absorbing material at this temperature and also because the temperature is too low to produce a large amount of CO gas by reaction (9).

4.1.3. Stage III

In Stage III, from about 300 to about 410 s the reduction rate increases reaching a maximum average value of 0.0045 g/s and then decreases. When the temperature of the mixture has reached about 1000°C, the production of CO gas by reaction (9) is accelerated and the reduction of wustite by reaction (8) also accelerates.

4.2. Reduction Temperature

Figure 5 shows the carbon plus oxygen (C+O) mass loss of the irradiated mixtures as a function of the registered temperature during the microwave irradiation period. The average transition temperature between the above discussed reduction stages with the corresponding deviations are indicated in the figure. Mass loss of all mixtures started below 220°C but since it was not possible to measure the temperature below this value the exact initial temperature of reduction can not be given. In the figure we can see that at a registered temperature of about 300°C the loss is already considerable and total reduction of magnetite to wustite finished at temperatures between 560 and 687°C, with an average of 651°C.

Table 1. Reduction reactions assigned to each peak shown in Figs. 4(b)–4(f).

| Peak | Reaction          |
|------|-------------------|
| 1    | 2Fe₃O₄ + C(9) → 6FeO + CO₂ |
| 2    | Fe₂O₃ + C(9) → 3FeO + CO   |
| 3    | FeO + CO → Fe + CO₂       |
| 4    | CO₂ + C(9) → 2CO          |
| 5    | FeO + CO → Fe + CO₂       |
| 6    | CO₂ + C(9) → 2CO          |
Reviews about the synthesis of inorganic solids using microwaves have been presented by Clark and Sutton\textsuperscript{5}) and Rao et al.\textsuperscript{6}) These reviews show that almost universally reactions under microwave irradiation occur faster and at lower temperatures than in conventional methods. In the case of the present investigation the carbothermal reduction of magnetite to wustite under microwave irradiation also occurred at lower temperature than in conventional heating therefore being within this frame.

Stage II started at an average registered temperature of 710°C and Stage III at about 1 020°C.

4.3. Reduction Mechanism of Magnetite to Wustite

Yun\textsuperscript{7}) indicated that two kinds of reduction, direct and indirect, were believed to take place within the blast furnace as follows. In direct reduction, solid carbon reacts directly with the iron oxide generating carbon monoxide together with a certain amount of carbon dioxide. This reaction was believed to occur at the tuyere zone. In the indirect reduction, carbon monoxide, which is formed by the combustion of carbon with the air blast at the tuyere level, reduces the iron oxides and carbon dioxide is formed.

Reduction of iron oxides employing solid carbon as the reducing agent with absence of volatile materials at temperatures around 1 000°C using conventional heating has been extensively investigated. It is generally accepted that the main reduction occurs through the gaseous intermediates CO and CO\textsubscript{2} but it is instructive to understand how the reduction starts. Rao\textsuperscript{8}) summarized the mechanism as occurring in three steps; initiation, propagation and termination. The initial formation of carbon monoxide is an important step in the overall reaction. In the initiation step CO gas can be produced by three different ways; 1) reaction of C\textsubscript{3} with oxygen of the entrapped air, 2) reaction of C\textsubscript{3} with oxygen gas released by the dissociation of the iron oxide and 3) by “true” direct reduction occurring at the points of contact between the carbon and the iron oxide particles. The propagation is accomplished with the reduction of the iron oxide by the CO gas with production of CO\textsubscript{2} and regeneration of CO by the Boudouard reaction. At moderately high temperatures (ca. 1 000°C) the overall process becomes limited by the availability of CO gas according to the Boudouard reaction. The reduction is terminated if one or both of the gaseous intermediates become unavailable to the solid reactants. The same author\textsuperscript{8}) indicated that the true direct reduction beginning at the points of contact between iron oxide and carbon particles may be visualized as follows; as oxygen is removed from the solid in the form of CO and CO\textsubscript{2}, islets of reduced iron appear on the oxide surface and eventually join together to form a continuous shell around the still unreduced oxide. Further reduction is assumed possible by the diffusion of carbon atoms through the reduced iron shell to the iron oxide interface. The interfacial chemical reaction involving oxide and carbon is presumed to occur relatively rapidly as compared to the diffusion process.

To avoid the occurrence of the indirect reduction, Yun\textsuperscript{7,11}) among other investigators, studied the direct reduction of ferric oxide by carbon in vacuum at temperatures between 700 and 1 100°C. The work of Yun revealed that carbon dioxide was predominant at all temperatures in the initial stages: but as time passed it decreased at a rate related to the temperature. The extent of direct reduction was considerable only above 900°C. This author also established that diffusion of iron ions within the oxide crystal, rather than the diffusion of carbon atoms into the iron oxide is the rate determining process in the reaction of ferric oxides.

Baldwin\textsuperscript{9,10}) studied the reduction of iron oxides by solid coke under nitrogen flow and proved that even though the reduction takes place mainly by gaseous reactions, a small but definite amount of solid–solid reaction between the oxide and carbon occurs.

The above findings of other researches prove that solid–solid reactions between iron oxides and carbon occur and support the proposed initial reactions shown in Table 1 as the most feasible explanation to explain the results of the present investigation. The occurrence of solid–solid reactions is also supported by the fact that, the carbon used in the present work was 100% pure; therefore free from volatile material and the experimental system was purged with nitrogen gas until the partial pressure of oxygen reached a value of 1.0×10\textsuperscript{-4} atm. However, differently from the experiments carried out with conventional heating, under microwave irradiation the solid–solid reactions took place at much lower temperatures.

There are numerous experimental evidences about differences in reaction pathways and products due to microwave processing. These differences have been attributed to what is generically called, microwave effects. Commonly known potential benefits of microwave heating are caused by the volumetric nature of microwave energy deposition which provides, in particular, a possibility of faster and more controllable temperature ramp-up and its selectivity which can provide concentration of energy deposition in the desired region. These peculiarities of microwave heating can be treated as the thermal action of the electromagnetic field on matter. However, not all effects revealed in experiments can be explained within these notions.\textsuperscript{11}) The same author put forward the question; are the experimentally observed differences due only to a different heat deposition pattern, or do microwave electromagnetic fields play a role in it?

Considering the initiation steps presented by Rao\textsuperscript{3}) in the direct reduction of iron oxides by solid carbon and in view of the accumulated experimental evidences that materials which absorb microwave radiation are able to start the heating or to activate a chemical reaction, the following possible mechanisms are postulated to explain the experimental results of the present work.
The microwave electromagnetic field may induce the dissociation of magnetite, a highly microwave absorbing material, to produce oxygen gas that can react with solid carbon, another microwave absorbing material, to produce CO and CO₂ gases and/or 2) as also indicated by Rao “true” direct reduction may occur at the points of contact between the carbon and the magnetite particles. Under the microwave irradiation power of the present work, the reduction of magnetite to wustite at low temperature may occur mainly by one or both of these mechanisms. This reduction pattern can not therefore be explained to occur by thermal effects but by the so called microwave effects. At low temperature the CO₂ gas produced can not be used for the gasification of solid carbon and it is therefore lost. The CO gas produced at low temperature by the mechanisms already outlined can be used for the reduction same as in conventional heating but at a lower temperature. The microwave absorbing power of magnetite finishes at about 650°C and under the present experimental conditions; its reduction to wustite is accomplished below this temperature.

Liu et al., using very advanced experimental techniques, performed thermal investigations of direct iron ore reduction with coal in mixtures heated by radiation from a surrounding graphite cylinder under a constant heating rate of 10°C/min. The range of temperatures for each reduction presented by these authors is as follows; the reduction of Fe₂O₄ to FeO was between 740 and 870°C, but the reduction rate was lower between 740 and 800°C than between 800 and 870°C. FeO was subsequently reduced to Fe between 870 and 1 200°C but the rate of reduction was rapid between 950 and 1 100°C. It is therefore evident that under microwave irradiation reactions between magnetite and carbon black can occur at lower temperatures than under conventional heating. The results of the present work are in agreement with observations reported by other researches that the so call “microwave effects” can induce different chemical reaction patterns than the ones occurring under conventional heating.

5. Conclusion

The following conclusions were reached about the reduction of magnetite by carbon black under the present experimental conditions of microwave irradiation.

1) The reduction of magnetite to iron in carbon black mixtures under microwave irradiation was accomplished in three distinctive stages.

2) In the first stage, all the magnetite was reduced to wustite and some wustite to iron. The temperature at the start of the reduction was below 220°C and the mass loss occurred through a series of solid–solid as well as solid–gas reactions as shown in Table 1.

3) Total reduction of magnetite to wustite finished at temperatures between 560 and 687°C, with an average of 651°C.

4) After all the magnetite has been reduced and still there is available CO gas produced by the direct reduction of magnetite, reduction of wustite starts independently of the temperature, but the propagation is limited by gasification of carbon that is temperature dependent.

5) When the mixtures reach a temperature of about 1 000°C the production of CO gas from CO₂ by the Boudouard reaction becomes important and the reduction of wustite to iron speeds up.

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