Effect of Experimental Conditions on Cementite Formation During Reduction of Iron Ore Pellets

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Experiments have been carried out to study the effect of temperature, gas composition, residence time, and type of iron ore pellets on formation of cementite during gaseous reduction of hematite. Industrial iron ore pellets have been reduced isothermally in a gas mixture with H_2 and CO as main components. The presence of Fe_3C in the partially reduced pellets shows that reduction and cementite formation take place at the same time. The maximum content of cementite is identified in the samples reduced by H_2-CO at 1123 K (850 °C). The decrease in the carbide content due to addition of 1 pct CO_2 to the initial gas mixture reveals the major influence of carbon potential in the gas atmosphere. Further increase of CO_2 content increases the Fe_3C. The variations of the amount of cementite with the CO_2 content suggest that both the thermodynamics and kinetics of cementite formation are affected by the gas composition. Cementite decomposes to graphite and iron particles in reducing and inert atmospheres as the residence time of pellets at high temperature is increased above 60 minutes.

I. INTRODUCTION

THE growing interests in application of direct reduced iron (DRI) in electric arc furnace (EAF) have prompted several investigations of carburization of iron and formation of iron carbide during gaseous reduction of iron oxides.[1–5] The problems associated with metal dusting, a corrosion process taking place in iron and steels used in atmospheres with high carbon activity, have further emphasized the importance of studies in this subject.[6] Preceding works have shown that factors such as temperature, gas composition, total pressure in the reactor, and the residence time have great impact on the rate of formation and stability of carbides.[1–10]

Hayashi and Iguchi performed studies of carbide formation under different experimental conditions in H_2-CO gas mixtures with addition of sulfur.[1,2] They reduced and carburized four types of hematite ore with different compositions and concluded that carbide formation in the applied conditions was not influenced by the chemical composition of the ores. Addition of small amounts of sulfur to the gas mixture decreased the amount of carbon deposition and stabilized the cementite phase.[1] In another work, the rate of carburization was enhanced by application of higher gas pressures; however, it resulted in larger amounts of free carbon on the ore particles.[2] Similar results were obtained by Iguchi et al.[7] from carburization of iron in atmospheres containing CO, H_2, and H_2S. The rate of cementite formation increased at higher pressures and at higher temperatures in the fluidized bed. They discovered that the chemical reactions at the pore surface of reduced iron control the carburization rate. Although the presence of sulfur was beneficial to cementite formation and decreasing the carbon deposition, applying high sulfur activities in the gas decreased the rate of carbide formation. The rate of Fe_3C formation was largely influenced by the variations of CO content in the gas phase and maximum rate was achieved with 80 pct CO in the mixture.[7]

The decomposition and stability of cementite formed in CH_4-H_2-Ar atmosphere during reduction of iron ore at temperatures between 773 K and 1223 K (500 °C and 950 °C) were studied by Longbottom et al.[3] Cementite decomposition took place at all temperatures. They found out that under the experimental conditions applied, the cementite phase was most stable at temperatures between 1003 K and 1023 K (730 °C and 750 °C). The decomposition rate increased at temperatures below 873 K (600 °C) and above 1023 K (750 °C).[3]

Hwang et al. examined the carburization of pure iron powder, iron from reduction of hematite and iron sheets in H_2-CO atmospheres. They pointed out that the carburization kinetics are largely affected by the surface area of the iron powders and by mass transfer of carbon in the iron sheet. The iron obtained from gaseous reduction of Fe_2O_3 by H_2 had larger surface area and porosity than the pure iron powder. Therefore, the carburization rate was higher in the reduced iron powder.[8]

Grabke et al. conducted fundamental studies on the kinetics and mechanism of carbide formation and carbon deposition in iron in gas mixtures containing CO or CH_4 and traces of sulfur.[6] They concluded that the rate of carburization was higher in atmospheres containing CO than in CH_4. They also observed that the

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presence of sulfur prevented graphite nucleation and decomposition of cementite.

Due to the importance of the carbon and cementite contents in DRI, the present work has been performed focusing on the carburization taking place during gaseous reduction. The aim of this work is to investigate how the experimental conditions influence the formation of cementite during reduction of industrial iron ore pellets by gas mixtures containing H_2 and CO.

II. EXPERIMENTAL

A. Materials

Industrial iron ore pellets were reduced and carburized in the experiments. Two types of hematite pellets, named as type A and type B, were examined. The average porosities of type A and type B pellets were 26 and 34 pct, respectively. The average hematite content in both types was 96 pct and the pellets contained small amounts of nonferrous oxides such as SiO_2, Al_2O_3, CaO, and MgO. Detailed composition of the samples is not listed here to protect the interests of the providing company. Note that most of the experiments were carried out for type A pellets, while some experiments were conducted for type B to examine the effect of pellet properties on cementite formation.

B. Experimental Setup and Procedure

Isothermal reduction experiments were carried out in a thermogravimetric setup which is schematically depicted in Figure 1. Details of the apparatus and experimental procedure can be found in the previous publication.[11] The experimental procedure is briefly described here. In a typical run, a small basket made of Nikrothal 80 wire was used to hold the sample. The sample holder was connected to the balance using a stainless steel wire. The sample was positioned in the water-cooled chamber until the experiment started. The reaction tube was sealed with viton o-rings. High-purity argon gas with 1 L min^{-1} flow rate was passed through the setup. The furnace temperature was ramped up to the experimental temperature. After reaching the target temperature in the hot zone of the reaction tube, the argon gas was replaced by the reducing gas mixture with predetermined composition and flow rate. In order to reach an atmosphere with homogeneous composition, the gas mixture was passed through the reaction tube for 10 minutes. The sample was rapidly lowered to the hot zone of the furnace and reaction was started. The weight of the sample was recorded by the balance during reaction. When the sample reached a certain reaction extent, it was elevated to the water-cooled chamber rapidly. At the same time, gas mixture was replaced by high flow rate of argon gas to stop the reaction.

All experiments were performed with a constant flow rate of gas mixture, namely 1 L min^{-1}. Different gas compositions, reduction temperatures, and reaction times were applied. To identify the phases in the samples, X-ray powder diffraction (XRD) and
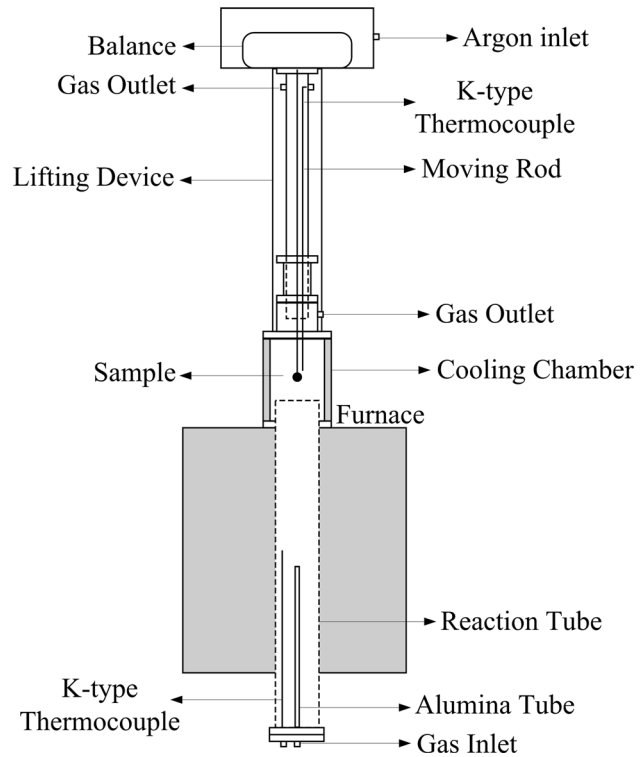

Fig. 1—Schematic illustration of experimental setup (the figure is adapted from Ref. [11]).

combustion analysis were applied. The XRD analysis of the grinded samples was performed using cobalt K_α radiation. Microstructural studies were performed using scanning electron microscopy equipped with energy-dispersive X-ray spectroscopy (SEM-EDS) and light optical microscopy (LOM). The quenched samples were carefully prepared for metallographic investigations. To distinguish the cementite phase, the freshly polished surface of the samples was etched by picral (4 vol pct picric acid in ethanol). The amount of cementite was evaluated by analysis of the images taken by LOM from the etched surfaces. The microscopic images were converted to black and white pictures in which the etched cementite phase was white and the rest of the matrix was black. These images were analyzed in MATLAB to estimate the ratio of the area of the white phase to the total area of the image. At least three images from each sample were evaluated and the average value was reported as the Fe_3C content.

III. RESULTS

The weights of the samples are followed using the TGA unit as shown in Figure 1. The situation is rather complicated since changes of weight are not only due to reduction, but also due to cementite formation and carbon deposition. Figure 2 presents the reaction curves for type A pellets reduced at 973 K and 1123 K (700 °C and 850 °C). Reduction at 973 K (700 °C) was accompanied by deposition of considerable amounts of free carbon on the sample; therefore, the reaction extent is

low at this temperature. Since the weight change from each reaction cannot be distinguished, the TGA results are not discussed in detail in the present work.

In the primary steps of this study, the presence of carbon and cementite in the reduced pellets was confirmed by combustion and XRD analysis. Further investigations were performed by microscopy and etching to identify cementite in the microstructure. The fraction of the total area of the cementite phase in the microscopic images was used to estimate the Fe_3C content of the samples. The estimated values were applied to compare the variations of the amount of carbide in the samples. To confirm the reliability of the results from image analysis, the estimated fractions of cementite were compared with the XRD results for type A pellets. It is worthwhile to mention that the measured values are, in general, in agreement with the results obtained from XRD.

The influences of reaction temperature, composition of reducing gas, residence time of the samples, and type of iron ore on the formation of iron carbide were examined. A number of samples were quenched after reaching certain reaction extents at 1123 K (850 °C),
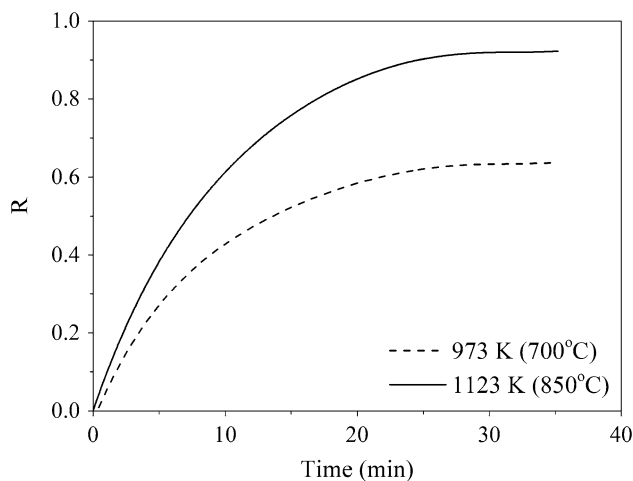
namely 0.5 and 0.8, and the Fe_3C content was estimated. Figures 3(a) and (b) present the optical micrographs of these two samples after etching. The cementite particles are tinted as white-bright yellow in the brown-blue colored matrix consisting of iron and unreduced oxides. The presence of cementite at these reaction extents is demonstrated in these figures. The figures indicate that the reduction of iron oxide and formation of Fe_3C take place simultaneously.

A. Effect of Temperature

The pellets were reduced isothermally at 973 K, 1123 K, and 1223 K (700 °C, 850 °C, and 950 °C) for 60 minutes by a gas mixture with fixed volume ratio of hydrogen and carbon monoxide ($H_2/CO = 1.5$). The average cementite contents obtained from the images are listed in Table I. The sample reduced at 973 K (700 °C) had smaller amount of Fe_3C than the sample reduced at 1123 K (850 °C). The content of cementite decreased when the temperature was increased from 1123 K to 1223 K (850 °C to 950 °C).

The photographs of the samples are shown in Figures 4(a) through (c). At 973 K (700 °C), large amount of carbon deposition completely covered the surface of the pellet (Figure 4(a)). At this temperature, the reduction slowed down when the thickness of carbon layer increased and the reduction of pellets was incomplete. Figure 4(b) presents the optical micrograph from the etched sample reduced at 1123 K (850 °C). The presence of cementite (white phase) is evidently seen. Figure 4(c) presents the micrograph of a sample reduced at 1223 K (950 °C) after etching. Small amount of cementite phase is shown in the figure.

B. Effect of Gas Composition

To study the effect of gas composition on cementite formation, various gas mixtures were employed at 1123 K (850 °C) for 60 minutes with a constant flow rate of 1 L min^{-1}. In the first series of experiments, the ratio of hydrogen to carbon monoxide was altered in the gas. The average amount of cementite in these samples is reported in Table II. The values show that increasing
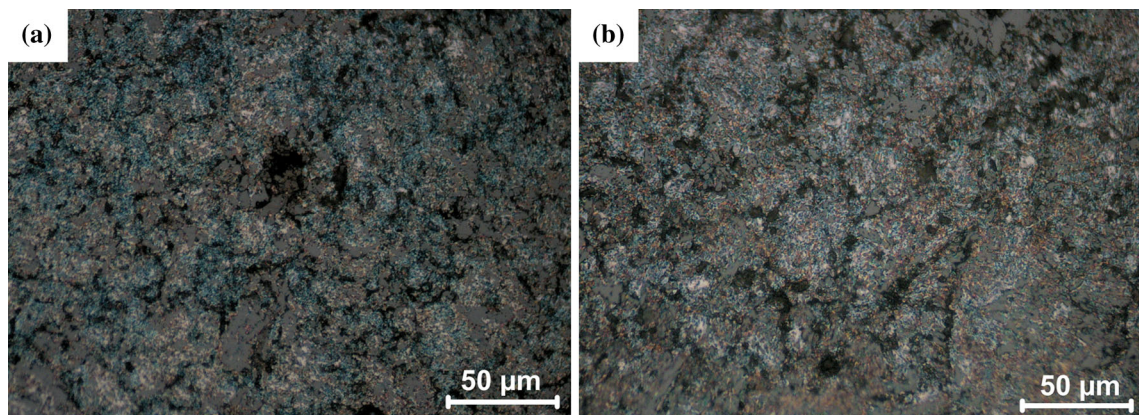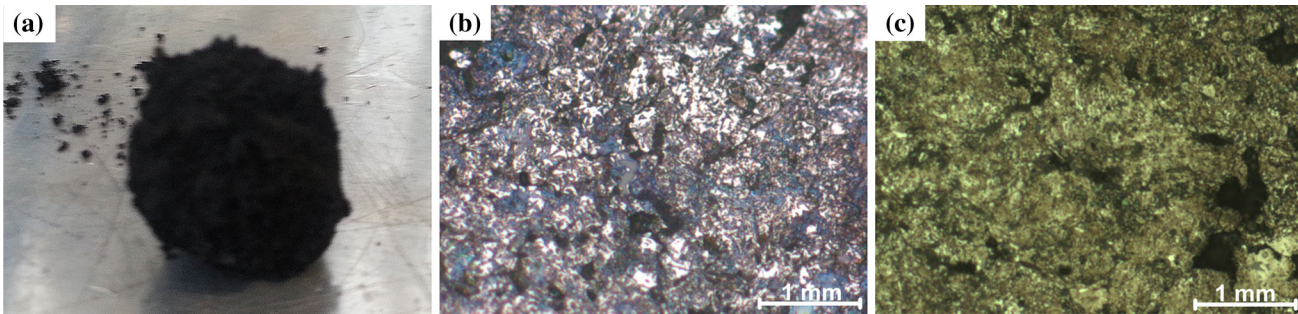

Fig. 2—Reaction curves of type A samples, $H_2/CO = 1.5$.

Fig. 3—Optical micrographs of etched surface of partially reduced samples; (a) reaction extent = 0.5, (b) reaction extent = 0.8.

Table I. The Fe₃C Contents of Pellets Reduced at Different Temperatures

Temp. [K (°C)]	P_{H_2} (Atm)	P_{CO} (Atm)	Time (min)	Fe₃C (Pct)
973 (700)	0.6	0.4	60	8
1123 (850)	0.6	0.4	60	24
1223 (950)	0.6	0.4	60	10

Fig. 4—Reduction and carburization at different temperatures; (*a*) T = 973 K (700 °C), (*b*) T = 1123 K (850 °C), (*c*) T = 1223 K (950 °C).

Table II. Comparison of the Fe₃C Contents of Pellets Reduced with Different H₂/CO

Temp. [K (°C)]	P_{H_2} (Atm)	P_{CO} (Atm)	Time (min)	Fe₃C (Pct)
1123 (850)	0.6	0.4	60	24
1123 (850)	0.667	0.333	60	26
1123 (850)	0.75	0.25	60	30

Table III. The Fe₃C Contents of Pellets Reduced by Gas Mixtures with Initial Addition of CO₂

Temp. [K (°C)]	P_{H_2} (Atm)	P_{CO} (Atm)	P_{CO2} (Atm)	Time (min)	Fe₃C (Pct)
1123 (850)	0.6	0.4	0	60	24
1123 (850)	0.594	0.396	0.01	60	8
1123 (850)	0.582	0.388	0.03	60	15
1123 (850)	0.54	0.36	0.10	60	22

the H₂/CO ratio in the gas mixture causes small changes in the cementite content of the reduced samples.

In the second series of experiments, different amounts of carbon dioxide were added to the gas mixtures with similar contents of hydrogen and carbon monoxide. Table III presents the fractions of the cementite phase in these samples. Addition of 1 pct of CO₂ to the gas mixture resulted in a noticeable decrease of the cementite content. On the other hand, further increase of CO₂ to 3 pct and 10 pct increased the Fe₃C content.

C. *Effect of Residence Time*

To investigate the effect of reaction time, the samples were kept in the hot zone of the reaction tube for different lengths of time, varying from 30 to 180 minutes. The reaction temperature was 1123 K (850 °C) in these experiments, and the gas composition and flow rate were kept constant. In one test, the reaction gas was replaced by pure argon after 60 minutes. Table IV shows the changes in the Fe₃C

content due to variation of residence time. The maximum amount of cementite is formed after 60 minutes of reaction. Increasing the time to 120 and 180 minutes results in lower contents of Fe₃C in the pellets, demonstrating the decomposition of Fe₃C. Similar results were obtained when the samples were kept in inert atmosphere for additional 60 minutes after reduction.

D. *Effect of Pellet Type*

Reduction experiments were also performed for type B pellets with higher porosity and lower basicity than type A. The total iron content was similar in both pellets. The reduction tests were carried out at 1123 K (850 °C) for 60 and 120 minutes at similar conditions applied for type A pellets. The amount of cementite formed in type B was similar to type A. The decomposition of Fe₃C was also observed in these samples. Although the results for the cementite content in both samples were similar, larger amounts of carbon deposited on the surface of type B samples after 120 minutes

Table IV.   The Changes of Fe₃C Content with Reaction Time

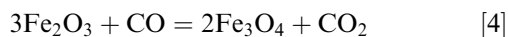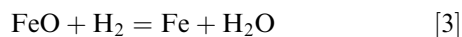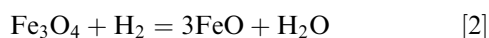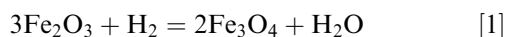| Temp. [K (°C)]	P_{H_2} (Atm)	P_{CO} (Atm)	Time (min)	Fe₃C (Pct)
1123 (850)	0.6	0.4	30	12
1123 (850)	0.6	0.4	60	24
1123 (850)	0.6	0.4	120	16
1123 (850)	0.6	0.4	180	11

Fig. 5—Carbon deposition in type B pellets reacted for 120 min at 1123 K (850 °C) in H_2-CO.

and the pellets disintegrated after this time. Figure 5 shows an example of type B pellet covered with carbon and cracked after 120-minute reaction.

IV.   DISCUSSION

Iron carbide formed in the samples with 0.5 and 0.8 reaction extents showed that reduction of hematite and formation of cementite occurs at the same time. Reduction of hematite by H_2 and CO takes place through Eqs. [1] through [6]. When the carbon activity, controlled by the CO content in the gas, becomes larger than unity, cementite forms through Eq. [7]. The chemical equilibrium in the system is affected by temperature, gas composition, and the chemical potentials of the species inside the pellet which are influenced by mass transfer in the solid phase. When the CO concentration at the reaction sites inside the pellets exceeds the equilibrium value, Eq. [8] shifts toward production of more CO_2 and solid carbon, resulting in higher carbon activities in the solid phase.

$$3Fe_2O_3 + H_2 = 2Fe_3O_4 + H_2O \qquad [1]$$

$$Fe_3O_4 + H_2 = 3FeO + H_2O \qquad [2]$$

$$FeO + H_2 = Fe + H_2O \qquad [3]$$

$$3Fe_2O_3 + CO = 2Fe_3O_4 + CO_2 \qquad [4]$$

$$Fe_3O_4 + CO = 3FeO + CO_2 \qquad [5]$$

$$FeO + CO = Fe + CO_2 \qquad [6]$$

$$3Fe + C = Fe_3C \qquad [7]$$

$$2CO = CO_2 + C_{(gr)} \qquad [8]$$
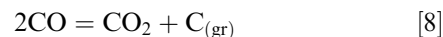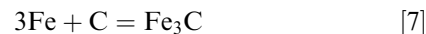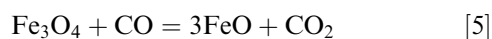
A. Effect of Reaction Temperature

Three different cases illustrated in Figure 4 showed the influence of temperature on carburization of type A pellets. The estimated cementite content (Table I) increased when the temperature increased from 973 K to 1123 K (700 °C to 850 °C).

It was observed in the present experiments that carbon deposition on the surface of pellets started from the initial stages of reduction by H_2-CO mixture at 973 K (700 °C). Similar results were obtained and discussed in the previous work.[11] Carbon deposition during reduction has been reported in other works which used gas mixtures containing H_2 and CO.[1,2,6,7,9] Formation of graphite takes place on the surface of pellets in atmospheres with high carbon potential. Reduced iron acts as a catalyst for carbon deposition; therefore, the amount of deposited carbon is enhanced as reduction proceeds.[11] The thickness of the carbon layer increases with time and slows down the diffusion of reducing gases to the pellets. Consequently, at 973 K (700 °C), carbon activity inside the solid is lower compared to 1123 K (850 °C), and less cementite is formed.

By increasing the reaction temperature to 1123 K (850 °C), carbon deposition was prevented in the initial stages of reaction, and larger amount of Fe₃C was identified in the samples. The absence of a thick carbon layer on the sample at higher temperature also eliminated the mass transfer resistance through this layer in the primary stages of reduction. Since the reaction gases could diffuse into the pellet without large mass transfer resistance, the chemical potential of carbon would be high enough to form cementite. The present results evidently show that avoiding the deposition of carbon at the initial stages of reduction is essential for increasing the amount of cementite in the reduced pellets.

Further increase of temperature to 1223 K (950 °C) resulted in smaller Fe₃C contents. At 1223 K (950 °C), the carbon activity in a gas mixture with fixed composition is lower and the driving force for carbide formation is decreased; therefore, less cementite is formed in the samples at this temperature. Additionally, cementite is less stable at higher temperatures and the decomposition rate increases. Therefore, lower amount

of Fe_3C at 1223 K (950 °C) can be attributed to the lower carbon activity and to higher rate of cementite decomposition at this temperature. The highest content of Fe_3C was identified at 1123 K (850 °C) after 60 minutes of reaction.

The present results clearly show that temperature has a twofold effect in this process. Higher reaction temperatures increase the reduction rate and mass transfer by formation of more and larger cracks and pores and provide higher surface area for reaction of carbon with reduced iron. On the other hand, higher temperatures lower the carbon activity in a gas mixture with fixed composition and decrease the driving force for carbide formation. Increase in temperature also results in faster decomposition of cementite. Therefore, the optimum condition for cementite formation is dependent on the experimental conditions and the system. Thus, it can be concluded that with the applied gas composition and flow rate, the optimum temperature for cementite formation in type A samples is 1123 K (850 °C). The optimum temperature for cementite formation strongly depends on the atmosphere composition.

B. Effect of Gas Composition

Changes in the ratio between hydrogen and carbon monoxide cause small differences in the Fe_3C content. The results in Table III show slight increase in cementite when the ratio of H_2 to CO in the gas is increased. Hayashi and Iguchi also reported that the amount of cementite after reduction is not influenced by the H_2/CO ratio in a certain composition range.[1]

As shown in Table II, the maximum cementite content is obtained when there is no initial amount of CO_2 in the reducing gas at 1123 K (850 °C). Adding 1 pct CO_2 resulted in large decline of the Fe_3C content. Further increase of CO_2 to 3 pct and 10 pct increased the amount of carbide.

Examination of the sample reduced by gas mixture containing 10 pct CO_2 by SEM-EDS showed that there is negligible amount of carbon covering the outer surface. Additionally, the amount of graphite in the inner parts of this pellet was smaller compared to the

sample reduced at the same conditions when there was no CO_2 added to the gas mixture. Figure 6 shows the backscattered images of these two samples at low magnifications.

It is evident from the results that the variation of CO_2 content in the gas atmosphere has a substantial influence on the carburization process. The reducing potential of the gas and the activity of carbon are affected by the presence of CO_2. Calculation of the thermodynamic activity of carbon in a gas mixture of H_2-CO-H_2O-CO_2 was performed previously by the authors.[11] The results showed that increasing the temperature at a fixed gas composition, and gradual increase of CO_2 (from 0.01 to 10 pct) at a constant temperature decrease the carbon activity in the gas mixture.

The fact that the amount of cementite decreases with 1 pct CO_2 addition and increases with addition of larger amounts of CO_2 strongly suggests that the effect of CO_2 is not only because of thermodynamics, but also kinetics. The reaction rates in Eqs. [1] through [8] depend on the local gas composition at a given temperature. The local gas composition in the reaction sites depends on (1) the gas composition of the bulk, (2) the mass transfer through the product layer, (3) the thermodynamic equilibrium of the reactions, and (4) the chemical reaction rates of these reactions. A clear understanding of the effects of these factors and their interrelationships would need further mechanism study and a realistic mathematical model of the reduction process.

C. Effect of Residence Time

The estimated values of cementite in the type A samples with reaction times from 30 to 180 minutes at 1123 K (850 °C) showed that the Fe_3C content was maximum after 60 minutes. The Fe_3C content gradually decreased when the samples were retained in the hot zone for longer durations of time. Furthermore, replacing the reducing gas by highly pure argon after 60 minutes of reaction and keeping the sample in inert atmosphere at high temperatures for additional 60 minutes resulted in lower cementite content. This
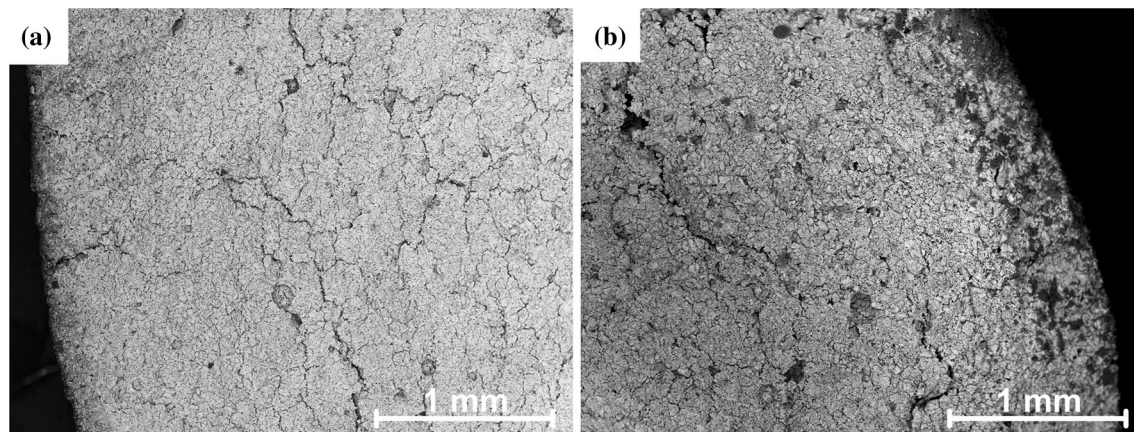

Fig. 6—SEM micrographs of type A pellets reduced at 1123 K (850 °C); (a) H_2-CO-10 pct CO_2, (b) H_2-CO.

indicated that the stability of Fe_3C in the solid phase is not affected by the carbon potential in the gas phase. Fe_3C is a metastable phase and it decomposes to iron and graphite by the backward reaction in Eq. [7]. Examination of the unpolished surface of samples by SEM-EDS illustrated the presence of iron-containing graphite particles in the pellets. Figure 7 shows a backscattered microscopic image of the sample reduced completely at 1123 K (850 °C) in H_2-CO mixture and kept at high temperature in argon atmosphere for additional 60 minutes. Fine iron particles dispersed in the graphite cluster can be seen in this figure, showing evidence of the cementite decomposition. Previous researches confirm that the decomposition of cementite by time takes place in both CO and CH_4 containing atmospheres.[2–4,6,7,9,10] Longbottom et al. reported that the rate of decomposition of Fe_3C in gas mixtures containing CH_4 changes at different temperatures and depends on the solid-state diffusion of carbon in iron.[3] The present results point out the importance of optimization of the process time with respect to the reduction time of iron oxide.

D. Effect of Pellet Type

The amount of cementite formed in type B iron ore pellet was similar to that of type A. However, after 120 minutes of reaction, type B pellets disintegrated and were covered by a thick layer of carbon (Figure 5). Comparable results were reported by Hayashi and Iguchi when different ores were reduced in H_2-CO mixture with small sulfur addition and similar amounts of cementite were formed in all ore types. They also observed deposition of large amounts of free carbon and swelling when no sulfur was supplied to the gas.[1] Although the degree of disintegration is one of the important characteristics for the iron oxide pellets, this aspect is not further studied in this work since it is not the main focus.

The experimental results and the above discussions have illustrated that carburization of iron oxide pellets depends on a number of factors: (1) pellet properties, (2) reduction temperature, (3) initial gas composition, (4) mass transfer (which is also dependent on the pellet characteristics), and (5) nonisothermal nature of the reactor. These factors are linked, both thermodynamically and kinetically. The correlation between these factors would determine the local gas composition at the reaction sites, which in turn holds the key of cementite formation. Therefore, optimization of the direct reduction process in a reactor would require a thorough understanding of interactions of different parameters and modeling of the same.

V. SUMMARY

An experimental study was carried out to examine the effect of experimental conditions, such as temperature, gas composition, reaction time, and type of pellet on formation of cementite during reduction of hematite pellets. Formation of cementite started from the initial stages of reduction as cementite was identified in the microstructure of partially reduced samples. The reaction temperature was found to have a significant effect on the amount of cementite. Changes in the ratio between hydrogen and carbon monoxide resulted in small differences in the Fe_3C content. On the other hand, addition of CO_2 to the reaction gas had a significant impact. The maximum cementite content was obtained when there was no initial amount of CO_2 in the reducing gas at 1123 K (850 °C). Adding 1 pct CO_2 resulted in large decline of the Fe_3C content. Further increase of CO_2 to 3 and 10 pct increased the amount of iron carbide. The results strongly suggested that the effect of CO_2 was not only because of thermodynamics, but also kinetics. Increasing the reaction time after 60 minutes of reduction led to decomposition of cementite, both in reducing and inert atmospheres. The optimum condition to reach the maximum cementite content in type A samples was 60 minutes of reaction at 1123 K (850 °C) in the H_2-CO gas mixture.
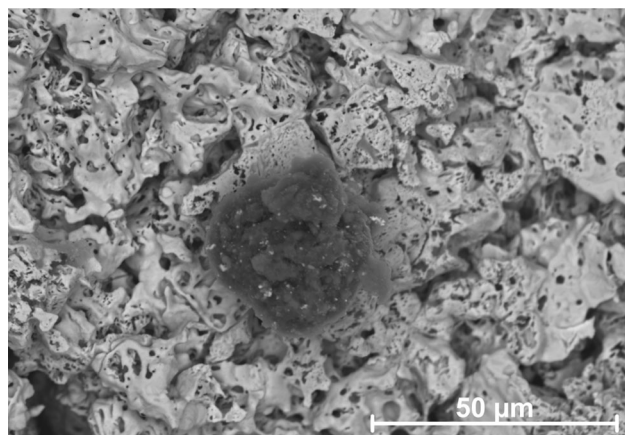
Fig. 7—SEM micrograph of graphite cluster in the sample reacted in H_2-CO for 60 min and kept in Ar for 60 min at 1123 K (850 °C).

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