Rate of Reduction of Ore-Carbon Composites: Part I. Determination of Intrinsic Rate Constants

O.M. FORTINI and R.J. FRUEHAN

A process for ironmaking was proposed consisting of the combination of a rotary hearth furnace and a bath smelter employing wood charcoal as reductant and energy source. This article examines reactions in composites of iron oxides and carbon at elevated temperatures in conditions developed to minimize the influence of mass and heat transfer to the overall rates. A combined reaction model considering the steps of carbon oxidation and reduction of the iron oxides was developed allowing the measurement of rate constants for carbon oxidation and wustite reduction to be used in a comprehensive pellet model developed in Part II of the current article. This analysis showed that wustite reduction can have a significant effect on the overall rate of reduction in composites at high temperatures or in the presence of large excess of carbon. Rate constants measured for graphite showed that graphite is as reactive as wood charcoal, possibly due to the catalysis of graphite or its higher temperature dependence. The poisoning of carbon surfaces by CO is less significant than anticipated from works of previous authors.

I. INTRODUCTION

THE productivity and energy efficiency of the iron blast furnace have increased significantly in the past 30 years. Energy consumption has been reduced from 40 GJ/tonne hot metal in the 1960s to less than 20 GJ/tonne in the 1990s. However, it still requires coke, produces about 1.5 tonnes of CO_2/tonne hot metal, and is highly capital intensive. If wood charcoal is used for iron production, net CO_2 and sulfur emissions can be significantly reduced. CO_2 is converted back to carbon and oxygen during tree growth and wood charcoal contains little sulfur. Wood charcoal is not appropriate to use in large blast furnaces of high productivity due to its low strength and density; commercial blast furnaces using wood charcoal are limited to 300,000 tonnes/year.

A new process has been proposed using composite pellets or mixtures of wood charcoal and ore fines in a rotary hearth furnace (RHF), which are melted in a smelting unit, as schematically shown in Figure 1. In the new process, composite pellets would be prereduced up to 75 to 80 pct metallization in the RHF and charged into a smelter for final reduction, gangue separation, and melting. This process overcomes the RHF drawbacks of low productivity and high gangue in the product by doing final reduction, melting, and gangue separation in the smelting unit. It overcomes the drawback of smelters, energy generation, by preheating and doing most of the reduction in the RHF. In order to fully evaluate and optimize this process, the rate of reduction, energy requirement, and gas generation in the RHF must be known.

The overall objective of this research is to develop and verify a model to compute the rate of reduction of ore-carbon pellets or mixtures including wood charcoal. The overall pellet model presented in Part II of this series of articles includes the rates of oxidation of the carbonaceous materials, reduction of wustite, heat transfer to and within the pellet, shrinkage, and other factors. In this article, the results obtained for determining the two rate constants for different types of oxide and carbon are presented. This model will then be used in a simulation of the RHF to evaluate and optimize the proposed process.

In theory, the rate of oxidation of carbon particles by CO_2 can be determined directly. However, in order to avoid mass-transfer effects, high gas velocities are necessary and it is never possible to ensure that such effects did not play a part in a given experiment. Moreover, at the high gas velocities necessary at elevated temperatures, the small powders of carbon and wustite would be carried away with the gas stream. Similarly, the direct measurement of the rate of reduction of the ore by CO would be difficult for the same reasons. Therefore, rate constants of carbon oxidation and wustite reduction were determined from measurements in mixtures and a combined reaction model considering the two steps of carbon oxidation and wustite reduction. The individual rate constants were determined by varying the relative amounts of carbon and wustite in different samples. In addition to preventing the interference of mass transfer effects, the direct measurement of rate constants in mixtures would take into account the possible interactions between reactants such as catalysis by newly formed iron. In Part II of this article, these results are used in a comprehensive model of an ore-charcoal pellet and experimental verification of the comprehensive pellet model is presented.

II. LITERATURE REVIEW

A vast amount of work has been done on the subjects of reduction in composites, carbon oxidation by CO_2, and reduction of iron oxides by CO. These three topics are of importance in studies of composites and a thorough review would extend far beyond the possibilities of a single text. Here, only a brief review of the most relevant studies on each subject is presented.
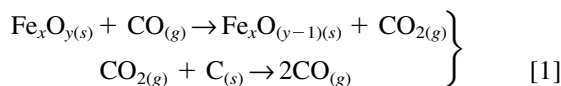
O.M. FORTINI, Senior Research Engineer, is with the U.S. Steel Research and Technology Center, Monroeville, PA 15146. R.J. FRUEHAN, Professor, is with the Materials Science and Engineering Department, Carnegie Mellon University, Pittsburgh, PA 15213. Contact e-mail: fruehan@andrew.cmu.edu

A. Reduction in Composites

A number of researchers have studied reduction in composites of iron oxides and carbon. It became a general consensus that the overall mechanism of reduction consists of two elementary steps of reaction schematically represented by

$$\left.\begin{array}{l} Fe_xO_{y(s)} + CO_{(g)} \rightarrow Fe_xO_{(y-1)(s)} + CO_{2(g)} \\ CO_{2(g)} + C_{(s)} \rightarrow 2CO_{(g)} \end{array}\right\} \quad [1]$$

where $x = 1$, 2, or 3
when $y = 1$, 3, or 4.

Fruehan[1] and Rao[2] studied reaction rates in composites with different types of carbons and found a good representation of data with a reaction mechanism dominated by the oxidation of carbon at lower temperatures. In the work of both authors, faster rates were measured in the presence of carbon oxidation catalysts such as lithium and slower rates in the presence of inhibitive agents such as sulfur reinforcing the argument of control by carbon oxidation. The studies of Rao[2] were limited to temperatures up to 1086 °C and used graphite as the only carbon type. Those of Fruehan[1] extended up to 1200 °C and encompassed more varied carbon sources: coal, coke, and coconut charcoal. In Fruehan's studies, a considerable slowdown of rates at temperatures above 1086 °C was reported and attributed to the possible contribution of wustite reduction to the overall rate. Later, Sun and Lu[3] developed models for higher temperatures where both steps of carbon oxidation and wustite reduction are given attention.

B. Carbon Oxidation in CO_2

Carbon oxidation is usually dealt with in the literature with complex rate laws with more than one reaction constant. The most widely accepted mechanisms are those proposed by Gadsby et al.[4] and Reif,[5] which result in a rate law for carbon oxidation with the form

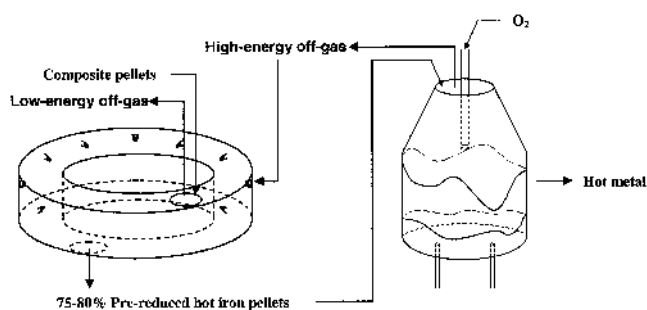$$R = \frac{k_1 P_{CO_2}}{1 + k_2 P_{CO} + k_3 P_{CO_2}} \quad [2]$$

Fig. 1—The proposed process.

In expression [2], the reaction rate per unit mass of carbon (R) is related to the pressures of carbon dioxide and carbon monoxide (P_{CO_2} and P_{CO}) by means of three constants k_1, k_2, and k_3. The interpretation of the rate constants k_1, k_2, and k_3 depends on the actual reaction mechanism. A number of authors have measured carbon oxidation constants based on a rate law such as Eq. [2]. Selected values can be taken from the extensive compilation of Story[6] and are given in Table I. In composite studies, however, carbon oxidation is usually addressed by means of a single reaction constant, as can be illustrated in the work of Sun and Lu.[3] This is reasonable since the gas composition and temperature ranges are relatively small. Therefore, the rate law for carbon oxidation in studies with composites may be written as

$$R_C = k_C m_C (P_{CO_2} - P_{CO_2}^C) \quad [3]$$

where R_C is the rate of carbon oxidation (g/s), k_C represents the rate constant of carbon oxidation per unit matter of carbon (g/g·s·atm), m_C represents the mass of carbon in the system (g), P_{CO_2} is the pressure of carbon dioxide in the system, and $P_{CO_2}^C$ stands for the CO_2 pressure in equilibrium with carbon at the temperature and pressure of the system at hand. Equation [3] implies that the surface area available for reaction is proportional to the mass of carbon so that it should be applicable to limited ranges of carbon burnoff. It should be noticed that the rate laws used in the works of Fruehan[1] and Rao[2] can be obtained from Eq. [3] in the particular case where a constant pressure of CO_2 is maintained during reduction. In light of Eq. [3], the temperature dependence or apparent activation energies (E_C) are clearly defined in terms of the change in k_C with temperature:

$$k_C = k_C^0 e^{-E_C/R_g T} \quad [4]$$

where k_C^0 is the pre-exponential Arrhenius factor (g/g·s·atm), R_g is the universal gas constant (atm·L/mol·K), and T is the absolute temperature (Kelvin).

C. Iron Oxide Reduction

In contrast to the complex laws used for carbon oxidation, the kinetics of wustite reduction seems controlled by the formation of a CO_2 activated complex on the surface of iron. Thus, reduction of wustite may be well represented as a first-order process based on the local pressure of carbon monoxide by means of a rate law such as that given by Turkdogan.[7]

$$R_{FeO} = k_{FeO} m_{FeO} (P_{CO} - P_{CO}^{FeO}) \quad [5]$$

where k_{FeO} is a specific rate constant (g/g·s·atm) obeying an Arrhenius relationship with temperature, m_{FeO} is the mass of wustite (g), P_{CO} is the pressure of carbon monoxide in

Table I. Rate Constants Measured According to the Mechanisms of Gadsby[4] and Reif[5] (After Story[6]); Apparent Activation Energies E_1, E_2, and E_3 are in Kcal/mol

	Temperature (°C)	k_1^0 (g/g·s·atm)	E_1	k_2^0 (atm^{-1})	E_2	k_3^0 (atm^{-1})	E_3
Coconut charcoal	734 to 839	1.32×10^8	58.8	1.26×10^{-8}	-45.5	3.16×10^5	30.1
Coke	800 to 1200	3.90×10^9	75.7	3.1×10^{-2}	9.70	5.91×10^{-6}	-17.6
Graphite	1060 to 1200	2.0×10^{14}	103.5	3.7×10^4	7.01	4.63×10^7	31.0
Anthracite coal	800 to 1090	4.37×10^2	32.5	4.6×10^{-3}	-16.9	1.8×10^{-3}	-16.6

the system, and P_{CO}^{FeO} is the pressure of CO in equilibrium with iron and wustite. As in the case of carbon, the area is considered proportional to the mass of wustite. Data on the intrinsic rates of reduction of wustite at lower temperatures are abundant in the literature. A temperature dependence of 40 Kcal/mol for the reduction of wustite can be estimated from the work of Turkdogan[7] at temperatures below 1050 °C. At higher temperatures, however, no reliable data from experiments where intrinsic rates are directly measured are available due to the influence of mass transfer.

III. MODEL DEVELOPMENT

In developing a model for reduction in composites taking into account the steps of carbon oxidation and wustite reduction, rate laws for the two elementary reaction steps were taken as Eqs. [3] and [5]. The use of such equations with no corrections for changes in carbon pore surface area available for reaction or more detailed descriptions for oxide reduction should restrain the use of this model to ranges of carbon burnoff and wustite reduction. Indeed, great changes in porosity may develop during reduction by wood charcoal or graphite seriously affecting measured values of intrinsic reaction rates per unit mass.[8,9] Nevertheless, this simplistic view may provide some insight into the interplay of carbon oxidation and wustite reduction occurring at high temperatures. The two rate laws in the form of Eqs. [3] and [5] can be used to compute the change in sample mass (m) with time (t) from the changes in the two solids as

$$\frac{dm}{dt} = \frac{MW_0}{MW_{FeO}} k_{FeO} m_{FeO} (P_{CO} - P_{CO}^{FeO}) + k_C m_C (P_{CO_2} - P_{CO_2}^{C}) \quad [6]$$

provided that the local pressures of CO and CO_2 are known. In Eq. [6], MW_i represents the molecular mass (g/mol) of component i. Since the volumes of gas produced are much larger than the volume of gas inside the sample:

$$P_{CO} = \frac{R_{CO}}{R_{CO_2} + R_{CO}} P_t \quad [7]$$

$$P_{CO_2} = \frac{R_{CO_2}}{R_{CO_2} + R_{CO}} P_t \quad [8]$$

where P_t is the total pressure inside the sample (atm). The net rates of production of CO and CO_2 in Eqs. [7] and [8] can be related to the rates of the individual reactions of wustite and carbon observing the stoichiometry of the individual reaction steps as

$$R_{CO} = 2 \frac{k_C}{MW_C} m_C (P_{CO_2} - P_{CO_2}^{C}) - \frac{k_{FeO}}{MW_{FeO}} m_{FeO} (P_{CO} - P_{CO}^{FeO}) \quad [9]$$

$$R_{CO_2} = \frac{k_{FeO}}{MW_{FeO}} m_{FeO} (P_{CO} - P_{CO}^{FeO}) - \frac{k_C}{MW_C} m_C (P_{CO_2} - P_{CO_2}^{C}) \quad [10]$$

Substitution of Eqs. [9] and [10] into Eqs. [7] and [8] allows the pressures of CO and CO_2 to be computed as functions of the specific rate constants and moles of reactants present at any instant in time as

$$P_{CO_2}^2/P_t + P_{CO_2} (1 + \phi - P_{CO_2}^{C}/P_t) = P_{CO_2}^{C} + \phi P_{CO_2}^{FeO} \quad [11]$$

$$P_{CO}^2/P_t - P_{CO} (2 + \phi + P_{CO}^{C}/P_t) = 2P_{CO}^{C} + \phi P_{CO}^{FeO} \quad [12]$$

The parameter ϕ in Eqs. [11] and [12] represents the relative importance of the two elementary steps of carbon oxidation and wustite reduction to the overall rate of reaction. The term ϕ is defined as the ratio

$$\phi = \frac{k_{FeO} MW_C m_{FeO}}{k_C MW_{FeO} m_C} \quad [13]$$

In the following treatment of reaction rates, constants for the two individual reaction steps are determined by simultaneously solving Eqs. [6], [11], and [12]. The numerical solution employed a fully explicit scheme to solve changes in number of moles of wustite and carbon with time. Equilibrium pressures of CO and CO_2 with carbon and wustite-iron were computed from Kubaschewsk et al.[10] and Darken and Gurry,[11] respectively. A total pressure of 1 atm was assumed due to the small sizes of samples used. The question of pressure buildup during reduction is controversial. Rao[12] derived a complex model, which predicted values as high as 20 atm for a sample depth of 2 cm. On the other hand, Tien and Turkdogan[13] argued that such pressure buildup could never be sustained since the powders would be blown away with the outgoing gas. Fruehan[1] measured pressure buildups by means of a manometer inserted into samples of artificial wustite and coke, coal or coconut charcoal and detected no significant pressure buildup. More recently, Lu[14] reinstated the problem as one nonverified hypothesis in many reduction models. Here, the option was taken to rely on the experimental measurements of Fruehan[1] and the argument of Tien and Turkdogan.[13]

IV. EXPERIMENTAL

In this work, wood charcoal was used as a reductant to represent the class of natural carbons. The wood charcoal used was characterized for ash and volatile content in separate sets of experiments prior to reduction. A volatile content of 21 pct in mass was determined in experiments of fast heating under argon. Experiments of oblivious burning of wood charcoal under CO_2 and air at temperatures higher than 850 °C revealed a very low ash content of less than 2 pct in mass. The reagent grade graphite used to represent the class of synthetic carbons had a purity of 99.9 pct or higher, as determined by the supplier.

Wustite obtained from taconite concentrate was used to represent the class of natural wustites. Gangue contents in the taconite concentrate used for preparation of wustite are in the range 4 to 6 pct in mass as determined by chemical analysis and X-ray fluoroscopy. Wustite was obtained by prereducing the original iron oxides at temperatures ranging from 1000 °C to 1050 °C under mixtures of 50 pct CO-50 pct CO_2. Prereduction to wustite was confirmed by the weight loss of the samples. Artificial wustite was obtained from reagent grade hematite with purity 99.9 pct or higher, as determined by the

provider following the same procedure of prereduction under CO-CO_2 at temperatures higher than 1000 °C.

All reactants used were sized to -200 mesh and thoroughly mixed into master mixtures of 4 to 5 g total mass. The masses of reactants used to prepare the master mixtures were measured to a precision of 10^{-3} g. Prior to preparing the master mixtures, all wood charcoal was devolatilized in an induction furnace under argon for 8 hours and complete volatile release confirmed by the total mass loss of the samples. In preparing the mixtures, account was taken of the ash and gangue contents in the wood charcoal and taconite.

In all reduction experiments, samples of 0.10 to 0.70 g from the master mixtures prepared were placed in a small alumina crucible (0.5-cm i.d., 2-cm high, 2.8 g). The mass change after the samples were quickly loaded into a hot furnace was monitored in an apparatus, as shown in Figure 2. The furnace temperature was calibrated prior to the experiments with thermocouples placed at several different positions along the hot zone and a safety margin of ± 10 °C adopted for the precision in the hot zone. Before each of the experiments, the gas inside the reaction chamber was purged with argon at a total flow rate of 2 L/min for 1 hour to avoid oxidation of carbon or wustite by residual oxygen. During this period, the samples were kept suspended above the furnace tube by means of a secondary chain linked to the crank mechanism shown in Figure 2. The purity of the gas before loading of the samples was confirmed by monitoring the composition with a mass spectrometer at the outlet of gas. After the purging period, the samples were quickly loaded into the furnace using the crank mechanism linked to the auxiliary chain. The auxiliary chain was released from the main chain once the samples were in the hot zone of the furnace. The balance was linked to a computer to continuously monitor the change in mass with time. This procedure of fast immersion was also used to determine the volatile content of wood charcoal as previously mentioned. The overall precision of the thermobalance was 0.003 g.
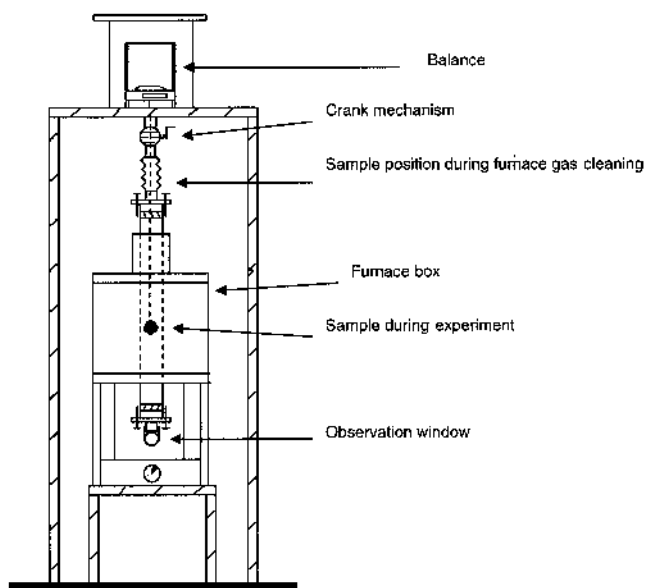
Conditions of heat transfer in the experimental furnace were studied using dummy samples of pure alumina powder with an embedded thermocouple in a crucible, as used in the reduction experiments. A large variability in heating rates was found depending on the state of the surface of the crucible indicating that most of heat transfer is due to radiation. Results from this analysis were used to estimate the heat supply to the samples during reduction and a maximum change of 5 °C in sample temperature induced by reactions was estimated for the sample sizes and furnace temperatures used.

V. RESULTS AND DISCUSSION

A brief discussion of the general features of our measurements can be helpful in the interpretation of reaction rate data and meaning of measured rate constants. Typical results of experimental measurements are shown in Figure 3. The measured curves exhibit a behavior quite similar to that described by Kohl and Engell.[15] In the most general case, the curves indicate the existence of three distinct periods with respect to the rates of reaction. After an initial period of constant sample weight necessary to bringing the sample up to the experimental temperature, a first onset of reaction at a slow rate can be identified. According to Kohl and Engell,[15] this period is associated with the buildup of gaseous intermediates at the points of contact between the
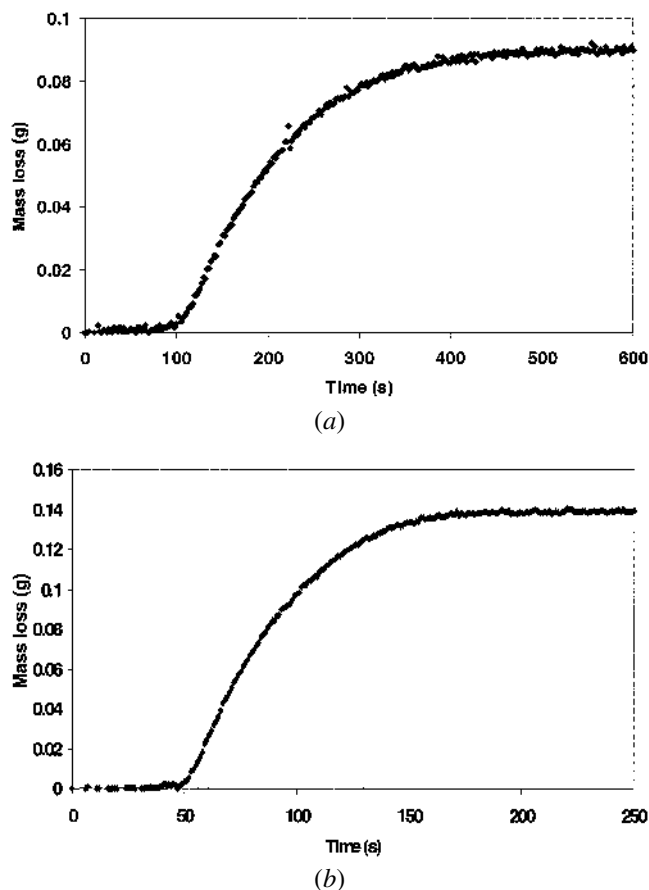

Fig. 2—Experimental apparatus.

(a)

(b)

Fig. 3—Typical results of measured mass change in samples with (a) wood charcoal and wustite from taconite and (b) graphite and wustite from hematite (1126 °C).

particles of iron oxides and carbon. In samples with graphite, this period may also be associated with the development of porosity in the initially compact carbon, as observed by Walker *et al.*[9] After the initial period of slow reaction, a main onset can be identified where the mechanism of gaseous intermediates operates fully. Here, as in most kinetic studies, the discussion is limited to the second and main period of reaction.

An example of determination of intrinsic rate constants is shown in Figure 4 for wood charcoal and wustite from taconite concentrate at a temperature of 940 °C. The procedure consists of starting with initial values for the two rate constants and iterates between the two experiments at low amounts of carbon and wustite until a good description of the data is found in both plots. After the initial determination of rate constants in experiments with low amounts of one of the reactants, samples with molar ratios of 1/1 were used for validation, as shown in Figure 5. The procedure used for determination of rate constants is schematically shown in Figure 6. Starting with a large excess of wustite, the rate of reduction is much faster than the rate of carbon oxidation so that the overall rate will suffer little influence from the rate of reduction of the oxide. Similarly, with excess carbon, the rate of carbon oxidation is faster than the rate of reduction and will be strongly influenced by the rate of
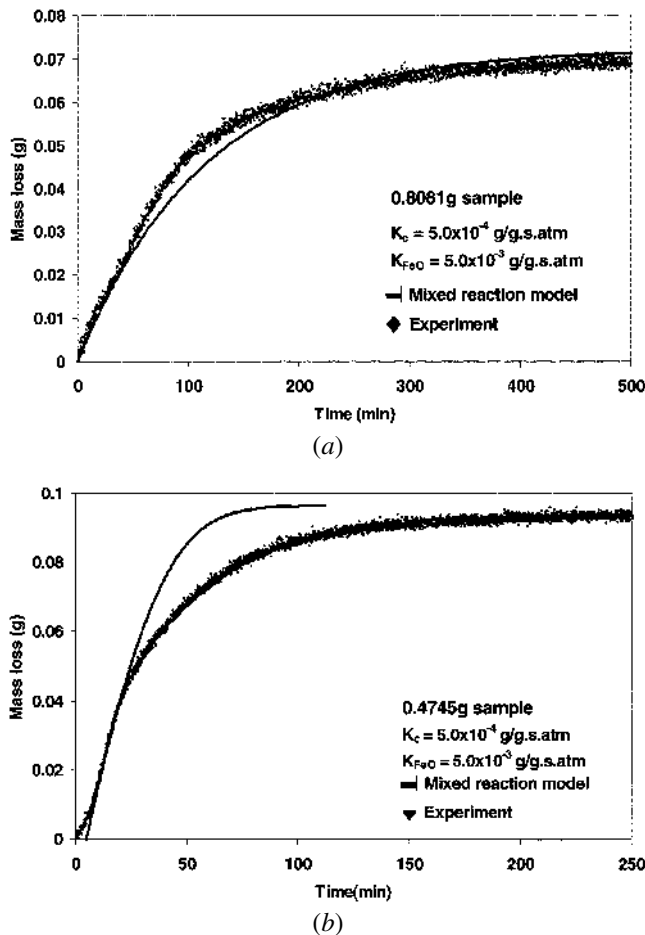
reduction of the oxides. At temperatures lower than 1086 °C, a good agreement could be found within 20 pct of the base values determined from the experiments with samples of molar ratios 1/5 and 5/1. Moreover, at such low temperatures, rate constants estimated for reduction of wustite from taconite concentrate or hematite are considerably higher than constants measured for wood charcoal and graphite, indicating a mechanism controlled mainly by the oxidation of carbon in agreement with Fruehan[1] and Rao.[2] Intrinsic rate constants for the reduction of wustites at temperatures lower than 1086 °C should be regarded as a minimum estimate. Since the overall rate under these conditions is primarily controlled by the oxidation of carbon, slightly lower values for reduction will not affect the overall rate.
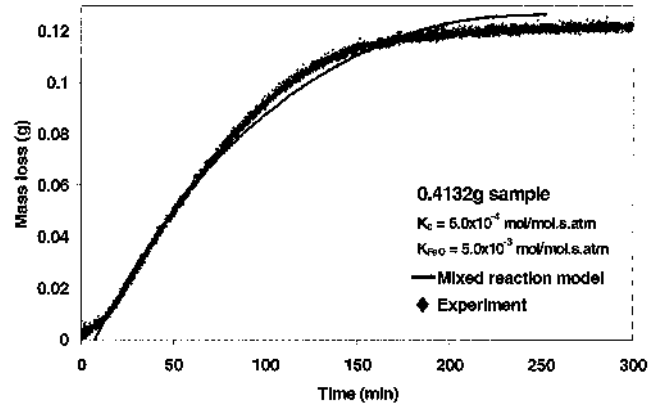
Fig. 5—Validation of rate constants determined from experiments with low amounts of reactants using equimolar samples of carbon and wustite. Results at 940 °C for wood charcoal and taconite concentrate.

Fig. 4—Iterative determination of rate constants by comparison of model results and measured mass losses at 940 °C in samples with (*a*) 1/5 carbon to wustite molar ratio and (*b*) 5/1 carbon to wustite molar ratio. Results for wood charcoal and taconite mixtures.
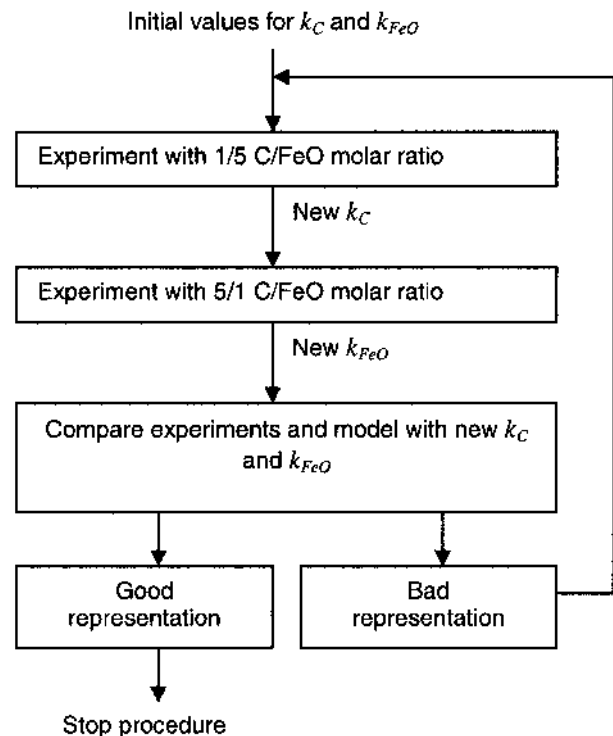
Fig. 6—Schematic of procedure for determination of rate constants in mixed control reaction model.

The importance of wustite reduction to the overall reaction mechanism seems to increase at temperatures higher than about 1086 °C. By following the same procedure for determination of rate constants as adopted at lower temperatures, larger deviations were found between constants determined in experiments with low amounts of reactants and equimolar mixtures of carbon and wustite, as exemplified in Figure 7. Nevertheless, the agreement found is within 30 pct on average; such agreement is surprisingly good in the face of the possible effects of wustite reduction to the overall measured rate. The contribution of wustite reduction may
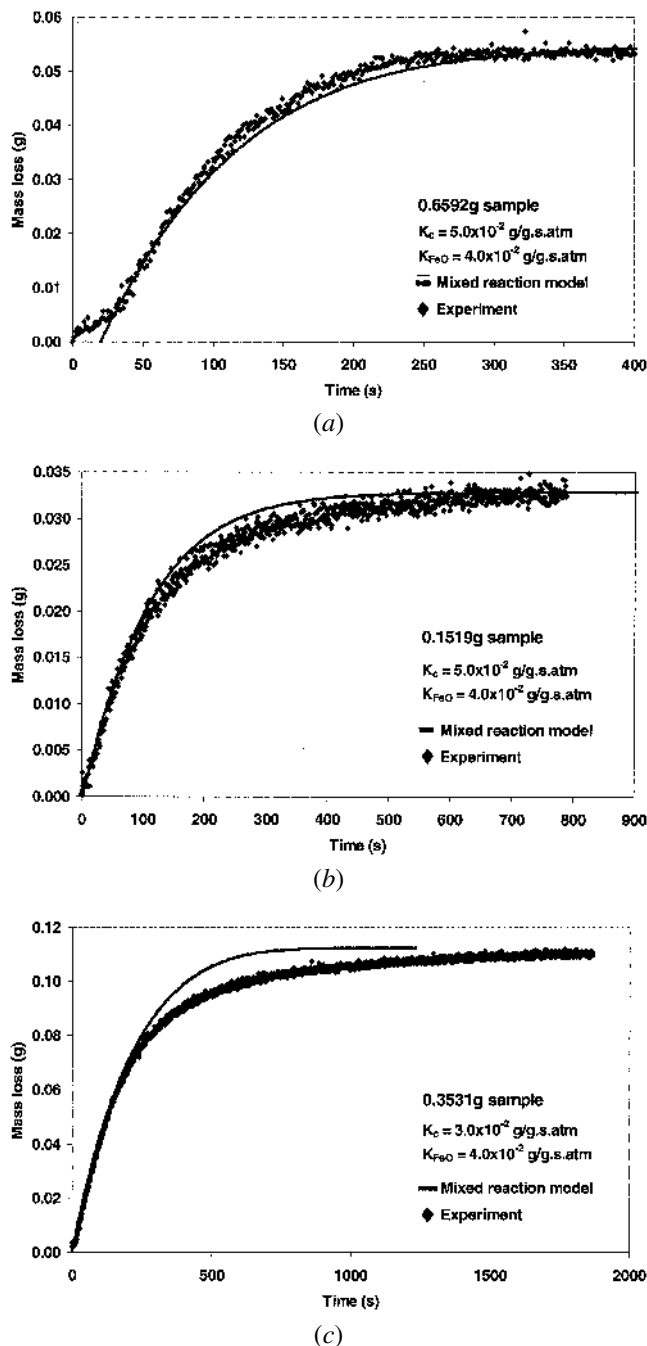

Fig. 7—Rate constants determined in composites of graphite with wustite from taconite. Molar ratios of (*a*) 1/5, (*b*) 5/1, and (*c*) 1/1. Furnace at 1126 °C.

have a twofold effect on the rates of oxidation of carbon: first, by limiting the availability of CO_2 for carbon oxidation, and second, by inducing poisoning of the carbon surface by CO, both factors contributing to a slowdown of intrinsic rates of carbon oxidation. In order to cope with this difficulty for the remainder of this analysis, the characteristic value considered for a given temperature was taken as the average between the experiments with large carbon excess and best fits attained by adjusting the value of intrinsic rates of carbon oxidation in equimolar samples. It should be noted that once wustite intrinsic rates become comparable to intrinsic rates of carbon oxidation, fittings of experiments with excess carbon become quite insensitive to the constants of the latter, thus granting some accuracy to constants determined for wustite. A final note should be put on the measured values of rate constants. In some experiments at low carbon to wustite ratios, it was not possible to attain a reasonable agreement between the measured mass loss and model results due to difficulties in defining the starting point of the second reaction zone discussed previously. In these cases, intrinsic rate constants were determined between the experiments with equimolar mixtures and low wustite. The average values of rate constants measured are shown in Table II. In spite of the broad ranges of apparent rate constants computed, analysis of Table II provides some useful observations. First, measured values indicate that reduction of wustite has a significant role in reduction at temperatures higher than 1086 °C and during the later stages of reduction in the presence of excess carbon. In industrial processes, an excess of carbon is most often found so that wustite reduction should play a significant role in the kinetics of reduction. As can be seen from Table II, values of constants measured for wustite from taconite at 1126 °C and 1186 °C are lower than those measured for wood charcoal, indicating that a shift in the rate controlling step from carbon oxidation to oxide reduction can take place in these types of composites at high temperatures. Second, comparison of the values obtained for graphite and wood charcoal at 1189 °C shows that the rates of oxidation of these carbons are comparable at high temperatures. In most of the literature, as exemplified by the work of Turkdogan and Vinters,[16] rates of graphite oxidation in CO-CO_2 mixtures are significantly slower than rates of oxidation of natural carbons such as coconut charcoal. However, Story and Fruehan[19] have previously shown that rates of oxidation of graphite become comparable to rates of oxidation of coke at higher temperatures due to the development of extensive porosity in graphite. Therefore, the measurement of comparable reaction rates at high temperatures could be due to the higher activation energy for graphite oxidation, development of extensive porosity, and catalysis of graphite by newly formed iron. The effects of catalysis would be less pronounced in samples with wood charcoal since this is already a more reactive carbon.

The temperature dependence of intrinsic rate constants determined for oxidation of wood charcoal is shown in Figure 8 along with the estimated experimental errors and data from other authors. In Figure 8, the comparison is presented between the values measured by Fruehan[1] for coconut charcoal and those measured here for wood charcoal. As can be seen in the figure, a linear trend is closely followed to 1126 °C but a marked difference is seen between 1126 °C and 1189 °C. This

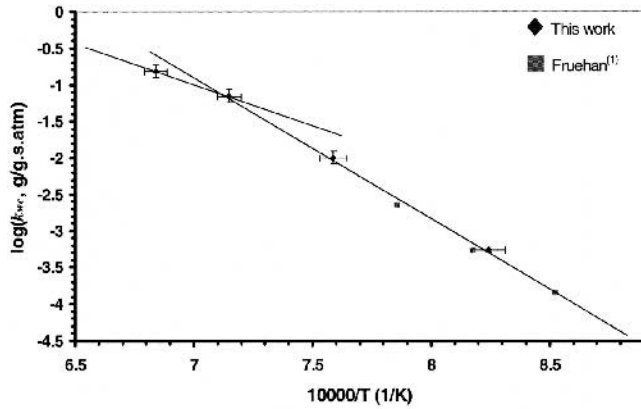| Temperature (°C)	Wood Charcoal	Graphite	Wustite from Taconite	Wustite from Hematite
940	5.5×10^{-4}	-×-	(5×10^{-3})	-×-
1045	1.0×10^{-2}	3.2×10^{-3}	4×10^{-2}	4×10^{-2}
1086	-×-	8.5×10^{-3}	-×-	6×10^{-2}
1126	7.0×10^{-2}	4.0×10^{-2}	4.0×10^{-2}	1.3×10^{-1}
1189	1.5×10^{-1}	1.5×10^{-1}	1.0×10^{-1}	3.5×10^{-1}

Fig. 8—Temperature dependence of rate constants for oxidation of wood charcoal. Rate constants from Fruehan[1] relative to coconut charcoal.

could be an indication of partial control by gas diffusion in the pores of carbon at higher temperatures. Indeed, the temperature dependence of 49 Kcal/mol computed with the experimental measurements at 1126 °C and 1189 °C is close to one-half the temperature dependence of 88 Kcal/mol computed with the measurements taken at lower temperatures. In the case of limited mixed control, also known as partial internal burn, where the rate of carbon oxidation is controlled by gas diffusion in pores and chemical reaction on the surface of pores, the rate constant k_C for carbon oxidation is given by[17,18,19]

$$k_C = \sqrt{k_S D_e \rho S} \qquad [14]$$

where k_S is the "true" kinetic constant of carbon oxidation per unit area, D_e is the effective diffusivity of reacting gas inside the pores of carbon, ρ is the bulk density of the carbon, and S is the specific area per unit mass of carbon. Since the effective diffusivity is not a strong function of temperature, values measured under partial internal burn usually result in temperature dependences of one-half the true temperature dependence of surface kinetics. For the present purpose of developing a model for reduction in composites, the question of determining the true temperature dependence of carbon oxidation is of secondary importance since the onset of partial internal burn seems limited to higher temperatures. For the purpose of estimating the magnitude of mass-transfer effects on the burning of carbon, the -200 mesh particles can be reasonably assumed as spheres of 2 μm in diameter since this is the largest diffusion distance possible in a given particle grain. Based on the porosity of typical artificial and natural carbons and measurements of gas diffusivity from other authors, a calculation indicates that rates controlled by mass transfer will be at least one order of magnitude faster than
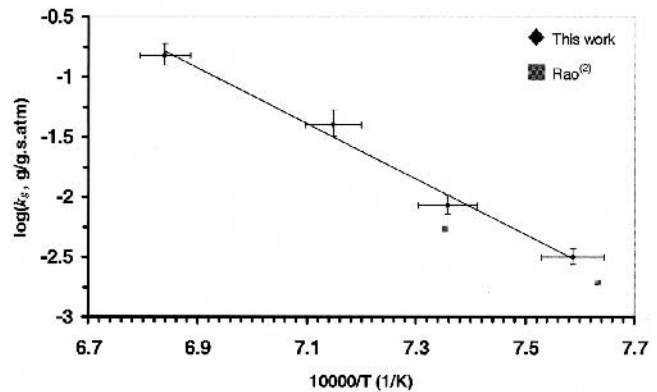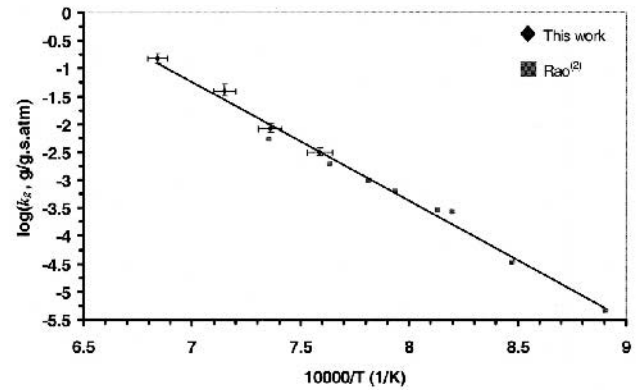

Fig. 9—Temperature dependence of rate constants for oxidation of graphite. Data from Rao[2] measured using amorphous graphite.

the measured rates, with the exception of experiments with natural carbons well above 1100 °C as corroborated by the present experimental results. Finally, the temperature dependence of 88 Kcal/mol obtained for wood charcoal at lower temperatures is close to the values of 81.2 and 84.1 Kcal/mol estimated from the works of Fruehan[1] and Turkdogan[16] for coconut shell charcoal. Figure 9 shows the temperature dependence of constants measured for graphite. For comparison, values measured by Rao[2] for amorphous graphite are also plotted. A temperature dependence of 106 Kcal/mol can be computed over the entire range of temperatures. This value is significantly higher than that measured for wood charcoal as should be expected from the states of graphitization of the two carbons.[16] It is also in good agreement with a value of 102 Kcal/mol estimated from the data compiled by Story.[6]

A comparison of rate constants measured here for reduction of wustite and literature values is difficult. First, as previously mentioned, most reported values are limited to low temperatures
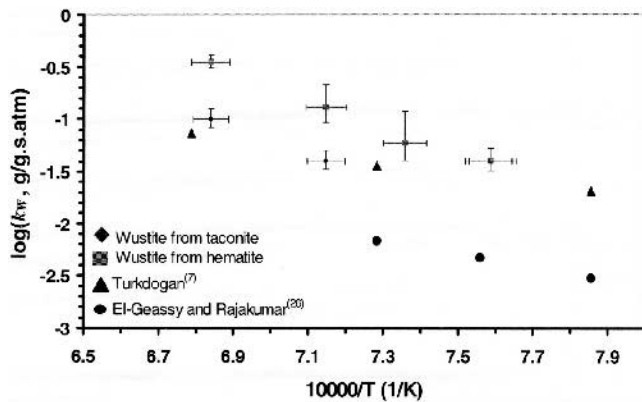
Fig. 10—Comparison of intrinsic rate constants for reduction of wustite measured in this work with values from the literature.

where the current method can provide only coarse estimates. Second, rate constants for reactions of CO and CO_2 on the surfaces of iron and wustite are usually reported per unit area of surface such as in the works of Grabke,[20] Pettit and Wagner,[21] Hauffe and Pfeiffer,[22] and Fruehan and Martonik,[23] among others. In other parts,[24,25] complex reduction models are used and rate constants fitted from experimental data relying on correlations for rate processes such as sintering and gas diffusion. In broad comparison, the values measured here are somewhat larger than those measured by Turkdogan and Vinters[7] and El-Geassy and Rajakumar,[26] as shown in Figure 10. However, both of these authors used methods of direct reaction with a stream of CO-CO_2 so that rates measured may be under considerable influence of mass transfer. The values measured here are more closely related to the conditions required in simulations of reduction in composites.

VI. CONCLUSIONS

For the evaluation of a new ironmaking process using an RHF and a smelter in series, it is necessary to have a model for the reduction of carbon-ore pellets. This model requires rate constants for reduction of FeO by CO and oxidation of carbon by CO_2. In the present study, these two rate constants were measured under the conditions of interest. In order to avoid the interference of mass-transfer effects, measurements were made on small samples of mixtures of fine wustite and carbon. The analysis of data and any reduction model for higher temperatures demands the use of a combined reaction model with regard to both reaction steps in the mechanism of gaseous intermediates. The use of this model, however, relies on the assumptions of constant surface area per unit mass of reactants and may be restricted to the initial period of reaction. The main findings of this research can be summarized as follows.

1. Wustite reduction rates become comparable to rates of carbon oxidation at higher temperatures. This is also important in composites with a large excess of carbon.
2. Graphite is about as reactive as wood charcoal at higher temperatures. This could be due to a higher temperature dependence of oxidation rates of graphite,[19] development

of extensive porosity,[19] and catalysis by newly formed iron.[1,2]
3. The CO poisoning of carbon surfaces is less significant than anticipated from measurements of other authors on carbon oxidation. In using a simple rate law for carbon oxidation, an average deviation of only 30 pct in intrinsic rate constants was measured.

In Part II of this series of articles, the results obtained here in terms of intrinsic rate constants as well as the combined reaction mechanism developed are used in a comprehensive model of a pellet, where effects of heat transfer become significant. In Part II of the current series of articles, experimental verification of the comprehensive model is also presented.

REFERENCES

1. R.J. Fruehan: *Metall. Trans. B*, 1977, vol. 8B, pp. 279-86.
2. Y.K. Rao: *Metall. Trans.*, 1971, vol. 2, pp. 1439-47.
3. S. Sun and W.-K. Lu: *Iron Steel Inst. Jpn. Int.*, 1993, vol. 33, pp. 1062-69.
4. J. Gadsby *et al.*: *Proc. R. Soc.*, 1948, vol. A193, pp. 357-76.
5. A.E. Reif: *J. Phys. Chem.*, 1952, vol. 56, pp. 785-88.
6. S.R. Story: Ph.D. Thesis, Carnegie Mellon University, Pittsburgh, PA, 1997.
7. E.T. Turkdogan and J.V. Vinters: *Metall. Trans.*, 1972, vol. 3, pp. 1561-74.
8. E.T. Turkdogan, R.G. Olsson, and J.V. Vinters: *Carbon*, 1970, vol. 8, pp. 545-64.
9. P.L. Walker, F. Rusinko, and L.G. Austin: *Adv. Catalysis*, 1959, vol. 11, pp. 133-221.
10. O. Kubaschewski, E.L. Evans, and C.B. Alcock: *Metallurgical Thermochemistry*, Pergamon Press, Oxford, UK, 1976.
11. L.S. Darken and R.W. Gurry: *J. Am. Chem. Soc.*, 1945, vol. 67, pp. 1398-1412.
12. Y.K. Rao: *Chem. Eng. Sci.*, 1974, vol. 29, pp. 1435-45.
13. R.H. Tlen and E.T. Turkdogan: *Metall. Trans. B*, 1977, vol. 8B, pp. 305-13.
14. J. Feinman and D.M. Rae: *Direct Reduced Iron Technology and Economics of Production and Use*, ISS, Warrendale, PA, 1999, p. 53.
15. H.K. Kohl and H.-J. Engell: *Arch. Eisenhuttenwes.*, 1963, vol. 6, pp. 411-18.
16. E.T. Turkdogan and J.V. Vinters: *Carbon*, 1970, vol. 8, pp. 39-53.
17. E.W. Thiele: *Ind. Eng. Chem.*, 1939, vol. 31, pp. 916-20.
18. A. Wheeler: *Adv. Catalysis*, 1951, vol. 3, pp. 249-327.
19. S.R. Story and R.J. Fruehan: *Metall. Mater. Trans. B*, 2000, vol. 31B, pp. 43-54.
20. H.-J. Grabke: *Z. Elektrochem.*, 1965, vol. 69, pp. 48-57.
21. F.S. Pettit and J.B. Wagner: *Acta Met.*, 1964, vol. 12, pp. 35-40.
22. K. Hauffe and H. Pfeiffer: *Z. Metallkd.*, 1953, vol. 44, pp. 27-36.
23. R.J. Fruehan and L.J. Martonik: *High Temp. Sci.*, 1971, vol. 3(3), pp. 244-56.
24. S.P. Trushenski, K. Li, and W.O. Philbrook: *Metall. Trans.*, 1974, vol. 5, pp. 1149-58.
25. M. Meraikib and H.A. Friedrichs: *Arch. Eisenhuttenwes.*, 1987, vol. 58, pp. 439-45.
26. A.A. El-Geassy and V. Rajakumar: *Iron Steel Inst. Jpn. Int.*, 1985, vol. 25, pp. 1202-11.