Smelting Reduction Mechanism of Fe–O–S Melts Using Solid Carbon

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The reduction of iron oxide in Fe–O–S melts by solid carbon was investigated to determine the reduction rate of iron oxide and to elucidate the reduction mechanism. The solid iron product deposits at the carbon surface, and grows towards the melt. On immersion of a graphite rod into the melt, the reduction rate reaches a maximum value and continues to stay at the value for some length of time, and then exhibits a gradual fall, followed by a constant residual rate. The temperature dependence of the rate is well represented by the Arrhenius equation, and the activation energy is 190 kJ mol\(^{-1}\) for 53.4 wt% FeO. The maximum rate shows a first order dependence on the FeO concentration, and is directly proportional to the geometric interfacial area between the graphite and the melt. Agitation of the melt hardly affects the rate of reduction. Solid iron produced at the graphite surface is very low in carbon, showing a ferritic structure. It is concluded that the reduction is controlled by the chemical reaction at the interface. The electrochemical reactions \(\text{Fe}^{2+} + 2e^- = \text{Fe} (s)\) and \(\text{O}_2 + 2\text{C(s)} = 2\text{CO(g)} + 2e^-\) take place and are responsible for the major portion of the reduction reaction until the carbon surface has been fully covered by the product iron. The dissolution rate of carbon from the graphite rod into the product iron is much slower than either the diffusion rate of carbon in the iron or the reaction rate of iron oxide by carbon diffused in the iron. This results in the product iron being very low in carbon and ferritic in structure.

KEY WORDS: smelting reduction; Fe–O–S melt; ironmaking; reaction rate; reaction mechanism; electrochemical reaction.

1. Introduction

Since global environmental protection regulations have become more stringent, every conceivable means must be explored to develop alternative iron and/or steel making processes which are more environmentally sound.

The liquid iron–oxysulfide (Fe–O–S) system has provided a possibility for the development of a novel process for smelting reduction of iron ore due to the existence of an extensive liquid miscibility gap at low temperatures and a low eutectic temperature of 920°C, its low viscosity and surface tension, and fast dissolution rate of wustite and hematite. It is therefore possible to carry out smelting reduction by using the Fe–O–S melt at low temperatures in the range of 1000 to 1200°C, and hence the reduction product will be solid iron. The low temperature operation would provide a number of added advantages in that the product would be free from contamination by gangue in the ore, and very low in carbon and sulfur, provided that the oxygen potential is carefully controlled. Referring to the Fe–Cu–O–S phase diagram, the use of Fe–O–S melt as a smelting reduction medium might also provide a possibility of recycling steel scrap containing high concentrations of copper which cannot be treated through conventional processes. Dissolution of steel scrap under an oxidizing atmosphere into the liquid Fe–O–S medium, and then reduction under a reducing condition will effectively remove copper from iron; dissolved copper ions will stay with the liquid medium while the iron ions are being reduced. Elliott outlined the possibility of using the Fe–O–S system as an iron smelting reduction medium, and, with his coworkers, has attempted to experimentally investigate some fundamentals including reduction rates of FeO dissolved in Fe–O–S melts.

In the present study, an attempt has been made to determine the reduction rate of iron oxide in Fe–O–S melts using solid carbon, and to elucidate the reduction mechanism at the melt/carbon interface.

2. Experimental

The experimental apparatus is shown schematically in Fig. 1. Iron–oxysulfides (Fe–O–S) were prepared by mixing FeO and FeS in appropriate ratios. Both FeO and FeS used in the present study were about 99.9% pure; impurities being mostly C, Si, P and Al. A total mass of 393 g of FeO and FeS mixture were melted in an iron crucible (54 mm ID×60 mm OD×250 mm L) under the inert atmosphere by flowing argon gas purified by passing through magnesium at 450°C. Most experiments were carried out at 1200°C, but the temperature range was extended up to 1300°C for some runs to find the effect of temperature. A
A graphite rod (20 mm in diameter and 200 mm in length) capable of rotation and vertical movement was attached to a holding device and positioned just above the melt surface. After homogenization of the Fe–O–S melt by holding for 20 min at the experimental temperature, and stirring the melt intermittently, the graphite rod was immersed into the melt. Reduction rates were determined by measuring the volumetric flow rate of the exit gases using a mass flow meter (model FM-360®, Tylan General). The signal from the mass flow meter was taken at one second intervals, and fed into the data acquisition software (Daqview®) installed in a computer. Dust in the exit gas stream was removed by passing it through a dust-filtering assembly (venturi type) installed between the exit of the furnace and the inlet of the mass flow meter. Experimental variables in the present study were temperature, melt composition, interfacial area between the melt and the graphite, rotation of the graphite rod, and bath stirring by blowing Ar gas. In the case of argon blowing, a graphite rod having a hole (2 mm in diameter) in the center was used. Table 1 summarizes the experimental conditions specified above. Immediately after the completion of each experiment, the melt sample together with the iron crucible was taken out of the furnace and quenched in water. Behavior of precipitation and growth of solid iron during the smelting reduction process was observed from the quenched samples using optical and scanning electron microscopes. The microstructure and properties of the iron produced were analyzed using various means including optical microscopy, scanning electron microscopy, electron probe microanalysis (EPMA), and microhardness testing.

3. Results

3.1. Reaction Characteristics

Figure 2 shows a typical result of the measurement of gas evolution as a function of time. Zero time was taken at the moment of immersion of the graphite rod into the Fe–O–S melt. It is seen that the whole process of gas evolution can be divided into four stages: the initial increase in the gas evolution rate (Stage I), a constant rate forming a plateau (Stage II) (hereinafter referred to as the maximum rate), the gradual decrease in the rate with time (Stage III), and finally a constant residual rate (Stage IV). Stage I was confirmed to be characteristic of the experimental system employed in the present work. In a separate experiment, CO gas was blown into the system with an empty crucible under otherwise exactly the same conditions as the runs with Fe–O–S melts, and the response pattern of the mass flow meter was monitored (the results are given in Fig. 3). It is clearly observable that the initial delay until the rate reaches its true value is due to the time required for the exit gas to travel through the path from the furnace tube, via the dust-filtering system to the mass flow meter. In order to understand the behavior at the remaining stages (Stage II–IV), the whole crucible assembly together with the graphite rod was taken out of the furnace at a number of different time intervals, and immediately quenched in water. From the

Table 1. Experimental conditions.

| Effects               | Temperature (°C) | FeO (mass%) | Interfacial area (x 10^-3 m²) | Rotation of Rod (rpm) | Argon blowing (cm³/mn) |
|-----------------------|------------------|-------------|-------------------------------|-----------------------|------------------------|
| Reference             | 1200             | 53.4        | 24                            | 0                     | 0                      |
| Effect of Temperature |                  |             |                               |                       |                        |
| 1225                  |                  | 53.4        | 24                            | 0                     | 0                      |
| 1250                  |                  | 53.4        | 24                            | 0                     | 0                      |
| 1300                  |                  | 53.4        | 24                            | 0                     | 0                      |
| Effect of composition |                  |             |                               |                       |                        |
| 1200                  |                  | 45.0        | 24                            | 0                     | 0                      |
| 1200                  |                  | 50.0        | 24                            | 0                     | 0                      |
| Effect of Interfacial area |              |             |                               |                       |                        |
| 1200                  |                  | 53.4        | 30                            | 0                     | 0                      |
| 1200                  |                  | 53.4        | 35                            | 0                     | 0                      |
| Effect of rotation of the rod |          |             |                               |                       |                        |
| 1200                  |                  | 53.4        | 24                            | 30                    | 0                      |
| 1200                  |                  | 53.4        | 24                            | 60                    | 0                      |
| Effect of bath stirring |                |             |                               |                       |                        |
| 1200                  |                  | 53.4        | 24                            | 90                    | 0                      |
| 1200                  |                  | 53.4        | 24                            | 0                     | 50                     |
| 1200                  |                  | 53.4        | 24                            | 0                     | 100                    |
| 1200                  |                  | 53.4        | 24                            | 0                     | 200                    |
sectioned specimens it was observed that solid iron was produced at the interface between the graphite and the Fe–O–S melt, and was growing towards the melt with time. Some examples of iron grown at the interface are shown in Fig. 4. It is clearly seen that solid metallic iron forms on the surface of the graphite rod. It is also seen that the amount of solid iron increases with time and hence the fraction of the graphite surface in direct contact with the Fe–O–S melt decreases (Figs. 4(a) and 4(b)). However, the general observation is that, although the above-mentioned fraction decreased, the gas evolution rate did not fall accordingly, but rather showed a tendency to stay at a constant value for some length of time (Stage II). Once the process has entered Stage III, the area available for direct reaction between the carbon and the melt is left very small (Fig. 4(b)). At Stage IV, the area for direct contact between the carbon and the melt is hardly seen, and hence the graphite rod is considered completely surrounded by the solid iron produced as a result of the reduction reaction. In summary, it appears that the fact that the reduction reaction occurs stage-wise is closely related to the availability and the extent of free interface for direct contact between the graphite and the melt. More systematic analysis of this phenomenon is deferred to the discussion section.

3.2. Governing Reactions

The overall reaction between carbon and iron oxide in the Fe–O–S melt can be expressed by the following equation:

\[
\text{FeO(melt)} + \text{C(s)} \rightarrow \text{Fe(s)} + \text{CO(g)} \quad \text{(1)}
\]

where FeO(melt) and C(s) represent FeO in the Fe–O–S melt and solid graphite, respectively. Direct contact between the melt and carbon will warrant the reaction given by Eq. (1) to take place. In the literature, where the reduction of FeO in oxide melts, i.e., slag, by carbon was studied, it has been suggested that the reaction given by Eq. (1) might proceed according to the following two steps:

i) At the melt/gas interface

\[
\text{FeO(melt)} + \text{CO(g)} \rightarrow \text{Fe(s)} + \text{CO}_2(g) \quad \text{(2)}
\]

ii) At the carbon/gas interface

\[
\text{C(s)} + \text{CO}_2(g) \rightarrow 2\text{CO(g)} \quad \text{(3)}
\]

Suppose that the direct reduction of iron oxide by solid carbon represented by Eq. (1) is dominant. Then the product iron will be seen to grow at the surface of the graphite rod. On the other hand, if the indirect reduction of iron oxide by carbon monoxide at the surface of gas bubbles represented by Eq. (2) was dominant, iron particles will form on the bubble surface, and then be either dispersed in the Fe–O–S melt or accumulated at the free surface of the melt. In the present study, nearly all of the iron produced was found to grow at the surface of the graphite rod, and iron particles were hardly seen either in the Fe–O–S medium or at the top surface. Figure 5 shows the cross section of the iron crucible one hour after immersion of the graphite rod into the Fe–O–S melt (53.4wt%FeO–46.6wt%FeS). It is seen that solid iron completely surrounds the graphite rod and grows towards the melt. No iron particles are seen in the Fe–O–S melt. In order to identify the shape of iron to be formed by the reaction given by Eq. (2), a separate experiment was carried out by blowing CO gas into the Fe–O–S melt. The
result is seen in Fig. 6 where the iron exists indeed in the particulate shape. The above observations strongly support the view that reduction of iron oxide in the Fe–O–S melt by carbon occurs mainly by the direct reduction reaction given by Eq. (1), and the indirect reduction reaction given by Eq. (2) occurs only to a negligible extent in the present experimental conditions. Some previous works reported in the literature on the reduction of iron oxide in oxide melts by solid carbon support the above view. Sugata et al. measured the rate of reduction of iron oxide in molten slags (5–90 wt% FeO) with carbon and CO gas, and found that the reduction rate by CO gas was less than 1% of that by solid carbon at 1350–1450°C. Sato et al. also found that the reduction of iron oxide by CO was negligible in comparison with the reduction by carbon. In a study on the reduction of molten iron ore by solid carbon, Takahashi et al. came to a conclusion that at temperatures higher than 1400°C molten wustite was reduced directly by solid carbon. Bafghi et al. measured the effect of CO gas formation on the reduction rate of iron oxide in molten slag by graphite, and concluded that the indirect reduction by CO gas was not as important as the direct reduction by graphite.

Based on the abovementioned discussion, the reaction rate is now calculated from the CO gas evolution rate. From the stoichiometry of Eq. (1), each mole of CO produced is equivalent to the production of one mole of iron, and it is possible to convert the volumetric flow rate of the off-gas into the molar reduction rate of iron oxide (FeO) using the following simple equation:

$$\frac{1}{A} \frac{dn_{FeO}}{dt} = \frac{1}{A} \frac{P}{RT} \frac{dV_{CO}}{dt} \quad \text{(4)}$$

where $A$ is the interfacial area ($m^2$), $n_{FeO}$ is the number of moles of FeO reduced (mol), $P$ is the ambient pressure (atm), $R$ is the gas constant ($82.057 \times 10^{-2} m^3 atm mol^{-1} K^{-1}$), $V_{CO}$ is the volumetric flow rate of CO gas in the exit stream ($m^3$), and $t$ is time (sec).

In the rest of this paper, the production rate or reaction rate will be given in terms of the number of moles of FeO reduced at unit interfacial area ($m^2$) and per unit time (sec).

### 3.3. Effect of Temperature

Figure 7 shows the effect of temperature on the rate of reduction of iron oxide in the Fe–O–S melts. It is seen that the maximum rate increases with temperature. The change with temperature of the maximum rate is given in Fig. 8 in the form of an Arrhenius type plot. It can be seen that the temperature effect is well represented by the Arrhenius equation and the activation energy for the reduction reaction of iron oxide in Fe–O–S melt (53.4 wt% FeO) by graphite is about 190 kJ mol$^{-1}$. Murthy et al. studied the reduction reaction of iron oxide in Fe–O–S melt, and re-
ported the activation energy of 287 kJ mol\(^{-1}\) for the melt composition of 45.5 wt% FeO. In the study of molten iron ore reduction with solid carbon, Takahashi et al.\(^{23}\) reported an activation energy of 234 kJ mol\(^{-1}\). On the other hand, Sato et al.\(^{15}\) found the activation energy of 314 kJ mol\(^{-1}\) and 130 kJ mol\(^{-1}\) for the reduction reaction of iron oxide by solid carbon using iron and alumina crucible, respectively. Seo et al.\(^{24}\) reported recently that the activation energy of reduction of pure FeO by solid carbon was 193.2 kJ mol\(^{-1}\). Sasaki et al.\(^{10}\) found from the study on the reduction of iron oxide in CaO–SiO\(_2\) slag with solid carbon that the activation energy was in the range of 68 to 119 kJ mol\(^{-1}\), depending on the basicity. In the study of the reduction rate of FeO in CaO–SiO\(_2\) slags by solid carbon, Min et al.\(^{22}\) found that the activation energy was 253 kJ mol\(^{-1}\) for 10 wt% FeO. It can be seen from the above that there is no consensus among the investigators on the activation energy for the reduction of iron oxide by solid carbon.

### 3.4. Effect of Melt Composition

**Figure 9** shows the change with time in the reduction rate of iron oxide in Fe–O–S melts of three different compositions. It is seen that the maximum rate increases with increasing FeO concentration in the melt. A plot of the maximum rate against the FeO concentration shows a linear relationship, as seen in [Fig. 10](#). The reduction reaction appears to follow first order rate kinetics. Murthy et al.\(^{2}\) also reported similar results with Fe–O–S melts in that the rate showed first order dependency on the FeO concentration.

### 3.5. Effect of Interfacial Area

The effect of the interfacial area between the carbon and the Fe–O–S melt was examined by measuring the rate with different immersion depths of the graphite rod into the melt. The results are given in [Fig. 11](#). It is seen that the rate increases with increasing the interfacial area, but the rate per unit interfacial area remains constant (see [Fig. 12](#)). Sato et al.\(^{15}\) and Hara et al.\(^{16}\) respectively observed similar results in their studies of reduction of iron oxide with solid carbon.

### 3.6. Effect of Bath Stirring

The influence of bath agitation on the rates of reduction reaction of Fe–O–S melts was examined in two different ways: by rotating the graphite rod and by blowing argon gas through a graphite tube. **Figure 13** shows the effect of rotation of the graphite rod on the rate of reduction of Fe–O–S melts. It is seen that the rotation of the rod exerts no influence on the maximum rate of reduction. The maximum rates with rotations of 30, 60

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**Fig. 9.** Change in FeO reduction rate with time at different initial FeO concentrations (1 200°C, area \((A) = 3.5 \times 10^{-3} \text{ m}^2\)).

**Fig. 10.** Effect of FeO concentration on the rate of reduction of FeO (1 200°C, area \(A = 3.5 \times 10^{-3} \text{ m}^2\)).

**Fig. 11.** Change in FeO reduction rate with time at different interfacial reaction areas between graphite rod and melt (1 200°C, FeO = 53.4 wt%).

**Fig. 12.** Effect of interfacial area on the rate of reduction of iron oxide by graphite (1 200°C, 53.4 wt% FeO).
and 90 rpm are the same, and show no difference in value from the rate of no rotation. However, the rotation of the rod resulted in a less pronounced decrease in the rate after the maximum rate. This result can better be understood from Fig. 14 which shows metallic iron formed in the vicinity of the graphite rod. It is clearly seen that the iron initially formed has been detached from the graphite surface due to rotation, and a new layer of iron product forms at the surface. When the graphite rod is immersed into the melt, solid iron will begin to form at the graphite surface, and at the same time the melt will be agitated due to the rotation. This will enhance the mass transfer in the melt. However, the maximum rate was observed to be independent of rotation of the rod (Fig. 13). Therefore it can be concluded that the mass transfer in the melt phase is not rate limiting. Sarma et al.\textsuperscript{21} reported that the reaction rate for slags containing iron oxide less than 10 wt% increased with increasing the rotating speed of the graphite rod. In a study with slags containing iron oxide, Sugata et al.\textsuperscript{8} observed that the rate increased until the rotation speed reaches 400 rpm, above which the rate became independent of the rotating speed. On the other hand, Sato et al.\textsuperscript{15} and Hara et al.\textsuperscript{16} have reported that, for slags containing iron oxide more than 10 wt%, the rate of reduction of iron oxide was hardly affected by the rotation of the graphite rod.

In a different attempt to enhance the mass transfer in the melt, a series of experiments were carried out by blowing argon gas into the melt. For these experiments, the solid graphite rod was replaced with the one (20 mm in diameter) having a hole (2 mm in diameter) in the center, and argon gas was blown through the hole while it was immersed in the melt. Figure 15 shows the results at three different flow rates; 50, 100 and 200 cm\textsuperscript{3} min\textsuperscript{1}. It is seen that the reduction rate decreases with increasing the argon flow rate, i.e., the intensity of stirring. This is believed to be due to the phenomenon that, as the argon flow rate increases, the fraction of the interfacial area occupied by argon gas bubbles increases, and hence the area available for direct contact between the carbon and the melt decreases. Murthy et al.\textsuperscript{21} made an observation similar to this.

### 3.7. Properties of the Iron Product

Figure 16 shows the microstructure of the metallic iron produced on the graphite surface. It is of interest to know that although the metallic iron grows directly on the graphite surface, no pearlitic structure is seen at all. Hardness of the metal measured by using a microhardness tester showed the values of about 100. The above observations support that the structure of the metal is ferritic.

### 4. Discussion

The experimental results given in the preceding section can be summarized as follows:
(1) Reduction of iron oxide in Fe–O–S melts by solid carbon occurs by direct reaction between iron oxide and solid carbon, and the indirect reduction by CO gas is insignificant.

(2) The product of the reduction reaction is solid iron, which forms at the interface between the graphite and the melt, and grows towards the melt.

(3) On immersion of graphite rod into the melt, the reduction rate reaches a maximum value and continues to stay at the value for some length of time, and then exhibits a gradual fall, followed by a constant residual rate.

(4) Temperature dependence of the rate is well represented by the Arrhenius equation, and the activation energy is 190 kJ mol\(^{-1}\) for 53.4 wt% FeO.

(5) The maximum rate shows a first order dependence on the FeO concentration.

(6) The maximum rate is directly proportional to the geometric interfacial area between the graphite and the melt.

(7) Agitation of the melt hardly affects the rate of reduction.

(8) Solid iron produced at the graphite surface is very low in carbon, showing a ferritic structure.

The observations of high activation energy (4) and no effect of bath agitation on the rate (7) immediately rule out the mass transfer in the melt as a candidate for the rate controlling step under the present experimental conditions. Therefore, the overall rate must be limited by chemical reaction(s) occurring at the interface, as the reaction product (solid iron) forms mostly at the interface (2). Then the above observation (1) tends to support that the reaction given by Eq. (1) is rate limiting. Now, the task left on hand is to check if all other observations given in the above summary truly support the view that the reaction given by Eq. (1) is rate limiting.

4.1. Consideration of Reaction Mechanisms

If the reaction given by Eq. (1) is elementary and also rate limiting, the rate of reduction of iron oxide in the melt can be represented by the following equation:

\[
\frac{1}{A} \frac{dC_{\text{FeO}}}{dt} = k \text{FeO} \quad \text{(5)}
\]

where \(k\) (m s\(^{-1}\)) is the reaction rate constant for Eq. (1), \(A\) (m\(^2\)) is the interfacial area, and \(C_{\text{FeO}}\) (mol m\(^{-3}\)) is the concentration of FeO in the melt.

The above rate equation, Eq. (5), appears to satisfy the observations (5) and (6) in the above summary. In order to determine if Eq. (5) also satisfies the rest of the observations, (3) and (8), it is necessary to gain an insight into the interfacial reactions that are possible. Figure 17 schematically shows four different reaction mechanisms which can conceivably occur at the interface.

Mechanism I: Indirect Reduction via Gas Bubbles
This mechanism has already been ruled out from a candidate as a major reaction that takes place in the present study.

Mechanism II: Chemical Reaction of Eq. (1)
If this mechanism is operative, metallic iron will precipitate initially along the line contact of three phases (melt, carbon and gas). Once iron has been precipitated, its further growth will occur only at a point contact of four phases (melt, carbon, gas and metal). Nevertheless occurrence of this reaction, however slow its rate might be, is quite conceivable but the reduction by this mechanism is unlikely to account for the major proportion of the overall reduction reaction. Furthermore, this mechanism fails to explain the observation (3) in the above summary. According to this mechanism, the area that is occupied by iron product will increase as the reaction proceeds, and hence the fraction of the interfacial sites that are available for the reaction given by Eq. (1) decreases with time. Therefore, the overall reaction rate is expected to decrease with time, but the actual observation is different: the overall rate tends to stay at its maximum value for an extended length of time. One might argue that the indirect reaction (2) is possible to occur at the melt–gas–Fe(s) contact, and CO\(_2\) gas so generated is being ferried to the graphite surface where it is converted to CO, and the whole sequence is repeated. This mechanism will help the Fe product layer to grow, rather than producing Fe particulates. Based on our experimental results and report in the literature that the reduction of FeO in oxide melts by CO is negligible in comparison with the reduction by carbon,\(^6\) contribution of this mechanism to the overall reaction rate should not be significant.

Mechanism III: Electrochemical Reactions
Since the Fe–O–S melt is ionic in nature, and hence the iron oxide in the melt exists in the form of ions, \(\text{Fe}^{2+}\) and \(\text{O}^{2-}\), the interfacial reaction given by Eq. (1) can be assumed to proceed in an electrochemical manner:

Anodic reaction: \(\text{O}^{2-} + \text{C}(s) = \text{CO(g)} + 2e^- \quad \text{(6)}\)

Cathodic reaction: \(\text{Fe}^{2+} + 2e^- = \text{Fe}(s) \quad \text{(7)}\)

In this case, the cathodic and anodic reactions do not necessarily have to take place at the same site: Cathodic reaction can occur either at the carbon/melt interface or at the metal/melt interface, or at both interfaces, whereas the anodic reaction proceeds at the contact line of three phases of the melt, carbon and gas. Electrons can freely move through the graphite and metallic iron. If this is the case, and the cathodic reaction is much slower than the anodic reaction, then the occupation of interfacial sites by metallic iron will hardly affect the rate, as long as some sites are left available for the anodic reaction. A probable reaction procedure will
then be,
(1) The anodic reaction proceeds at some favorable sites at the interface, and generates electrons as well as CO gas.
(2) The cathodic reaction occurs over all other sites at the interface, including the sites of the carbon/melt and metal/melt interfaces.
(3) Both cathodic and anodic reactions proceed at a steady state, and the overall reaction rate stays at a constant value as long as the sites initially active for the anodic reaction remain unaffected (Stage II in Fig. 2).
(4) All the sites for the cathodic reaction at the carbon/melt interface have been used up and further cathodic reaction takes place at the sites of the metal/melt interface, and/or by invading the sites for the anodic reaction. As the sites available for the anodic reaction diminish, the overall reaction rate begins to decrease gradually (Stage III in Fig. 2).
(5) Eventually all the interfacial area has been covered by the product iron, and sites for either cathodic or anodic reaction are no longer available. Carbon for the reduction reaction can only be supplied by diffusion through the metallic iron. The reduction reaction by this carbon is responsible for the residual rate shown in Stage IV.

The above qualitative explanation is well in accord with the observation (3) in the summary and in Fig. 2. Next, further examination of the experimental results to see whether they all support this view is in order.

Figure 18(a) is the reproduction of Fig. 9, but includes all data points obtained at every one second interval, and Fig. 18(b) shows the integrated amount of metallic iron production with time. It is seen from Fig. 18(a) that for the melt of 45.0 wt% FeO Stage II terminates at about 20 min after immersion of the graphite rod. It is also seen from Fig. 18(b) that, for this time interval, about 1 kg m⁻² of iron has been produced. The amount of iron produced at termination of Stage II for the melt of 50 wt% FeO (about 17 min) is roughly the same as that for the melt of 45 wt% FeO. For the melt of 53.4 wt% FeO the time at which Stage II terminates is not clear, but is in the range of 7 to 11 min, and the amount of iron produced in the corresponding time range is 0.6–1 kg m⁻². Figure 19 shows for the effect of the interfacial area on the reduction rate. It is seen that the amount of iron produced per unit area at the termination of Stage II varies with the interfacial area: it increases with decreasing the interfacial area. This is partly attributed to the effect associated with the geometry of the graphite rod. It was found that the amount of iron precipitated per unit area was larger at the end part of the rod than at the side wall. The relative effect of irregular deposition of iron at the end of the rod will be larger for the case of shallow dipping, i.e., of smaller total interfacial area. However, this end effect cannot account for all the differences shown in Fig. 19, as the surface fraction of the end part is mere 10–15% of the entire dipping surface. Other sources which are responsible for the rest of the differences are not immediately clear, but inherent experimental uncertainty may be one of the them. In summary, the amount of iron produced per unit interfacial area by the time when Stage II ends is roughly the same, irrespective of the melt composition and the interfacial area.

In order to explore further evidence that the cathodic reaction, Eq. (7), can occur at a different site from that of the anodic reaction, Eq. (6), an additional experiment was conducted, in which the graphite rod was allowed to touch the iron crucible during Stage III. The result is given in Fig. 20. It is of interest to notice that metallic iron grows on the wall of the iron crucible. This never happened when the graphite rod did not touch the crucible (Fig. 5). The above observation proves that the cathodic reaction actually takes place at
the wall of the iron crucible. Recently, Woolley et al.\textsuperscript{25} studied the reduction kinetics of CaO–SiO\textsubscript{2}–Al\textsubscript{2}O\textsubscript{3} slags containing up to 8 wt\% FeO, and reported that the reduction of iron oxide from slag by carbon in iron occurs as separate anodic and cathodic reactions; the locations of these reactions may be physically separated by macroscopic distances, and hence the overall reaction is an electrochemical reaction.

In short, existence of Stage II in the change of the reduction rate with time in the present study supports the view that the overall reduction reaction of iron oxide in Fe–O–S melt, Eq. (1), occurs, at least partly, in an electrochemical manner represented by Eqs. (6) and (7).

Mechanism IV: Reaction with Carbon Diffused through Metallic Iron

It is of interest to know that the metallic iron produced on the surface of the graphite rod is extremely low in carbon as seen in Fig. 16. A question now arises as to how the solid iron which touches carbon at one side and the Fe–O–S at the other can possibly be very low in carbon. One conceivable postulation is that the dissolution rate of carbon into the iron at the carbon/metal interface is much slower than either the diffusion rate of carbon in the solid iron or the chemical reaction rate between carbon in iron and iron oxide in the melt at the metal/melt interface. If this is the case, the residual rate of reduction at Stage IV shown in Fig. 2 is in fact the rate at which the reduction between the carbon transported through the solid iron and iron oxide in the melt, the rate-limiting step of which is the dissolution of carbon at the carbon/metal interface.

Using the results given in Fig. 9, the carbon dissolution rate is calculated to be 5×10\textsuperscript{-3} mol C m\textsuperscript{-2} s\textsuperscript{-1}. Since the diffusivity of carbon in γ-iron at 1 200°C is known to be about 5×10\textsuperscript{-10} m\textsuperscript{2} s\textsuperscript{-1},\textsuperscript{26} and the average thickness of solid iron layer on the graphite surface is 70–130×10\textsuperscript{-6} m (0.6–1 kg m\textsuperscript{-2}), the concentration gradient of carbon required to transfer 5×10\textsuperscript{-3} mol C m\textsuperscript{-2} s\textsuperscript{-1} can be calculated using the Fick’s first law equation:

\[ J_C = -D_C \frac{dC}{dx} = -D_C \frac{\Delta C}{\delta} \]  

(8)

where \( J_C \) is the molar flux of carbon in Fe (mol C m\textsuperscript{-2} s\textsuperscript{-1}), \( D_C \) is diffusivity of carbon in iron, \( C \) is the concentration of carbon in iron (mol m\textsuperscript{-3}), \( x \) is the diffusion distance (m), and \( \delta \) is the thickness of the iron layer (m).

Substituting the corresponding values into the equation, the concentration gradient to be established in the iron layer (\( \Delta C \)) is found to be 700–1 300 mol C m\textsuperscript{-3} or 0.1–0.2 wt\%. If the iron concentration at the metal/melt interface is negligibly low, the carbon content in iron at the carbon/metal interface is mere 0.1–0.2 wt\%. These low values of carbon concentration warrant the iron product being solid even at the carbon/metal interface, which was actually the case in the present study.

Considering the qualitative agreement of the above analysis with the experimental results, it can be concluded that the reduction of iron oxide by the carbon transferred through the metallic iron layer is operative at Stage II and III, and responsible for the residual rate of reduction at Stage IV. Due to inherent uncertainties involved in the above considerations and calculations, however, the conclusion given here should be considered tentative.

4.2. Overall Process of Reduction Reaction

It is now clear that the reduction of iron oxide in the Fe–O–S melt by solid carbon occurs by several reaction mechanisms operating in parallel. Dominating reaction mechanisms vary with time. Described below is the most conceivable reaction sequence that the overall process is likely to follow:

1. On immersion of the graphite rod into the Fe–O–S melt, Mechanisms II, III and IV are all operative, but Mechanism III (electrochemical reaction) dominates—Stage II.
2. Time eventually reaches a point at which all the sites other than those for the anodic reaction have been exhausted. Beyond this point, the cathodic reaction gradually invades the sites for the anodic reaction, and hence the overall rate experiences a gradual fall—Stage III.
3. Finally all the anodic sites have also been exhausted, and hence Mechanism IV is the only one that remains operative—Stage IV.

The above description adequately explains the experi-
mental observations made in the present study.

4.3. Applicability

Inherent advantages of the Fe–O–S system for use as a smelting medium of iron oxide ores have already been explained in the introduction section: low liquidus, high dissolution rate of iron oxides, low viscosity, low surface tension, and production of relatively pure iron. Furthermore, the iron oxide reduction rate in the Fe–O–S melt is quite lower than those for oxide melts (1400–1575°C). As far as the reaction rate is concerned, therefore, use of Fe–O–S medium for smelting reduction of iron ore can safely be justified. However, it is necessary to study how to control the morphology of the solid iron produced and how to collect them. If the solid iron can be consolidated directly into products, the conventional steps of melting, refining and solidification would be avoided.  

5. Conclusions

The reduction of iron oxide in Fe–O–S melts by solid carbon was investigated to determine the reduction rate of iron oxide and to elucidate the reduction mechanism. The observations are summarized in the following:

(1) Reduction of iron oxide in Fe–O–S melts by solid carbon occurs by direct reaction between iron oxide and solid carbon, and the indirect reduction by CO gas is insignificant.

(2) The product of the reduction reaction is solid iron, which forms at the interface between the graphite and the melt, and grows towards the melt.

(3) On immersion of graphite rod into the melt, the reduction rate reaches a maximum value and continues to stay at the value for some length of time, and then exhibits a gradual fall, followed by a constant residual rate.

(4) Temperature dependence of the rate is well represented by the Arrhenius equation, and the activation energy is 190 kJ mol⁻¹ for 53.4 wt% FeO.

(5) The maximum rate shows a first order dependence on the FeO concentration, and is directly proportional to the geometric interfacial area between the graphite and the melt.

(6) Agitation of the melt hardly affects the rate of reduction.

(7) Solid iron produced at the graphite surface is very low in carbon, showing a ferritic structure.

From the experimental results, the following conclusions have been drawn:

(1) The reduction reaction is controlled by chemical reaction at the interface.

(2) Electrochemical reaction of Fe²⁺ + 2e⁻ = Fe (s) and O²⁻ + C(s) = CO(g) + 2e occurs and is responsible for the major portion of the reduction reaction until the carbon surface has fully been covered by the product iron.

(3) The dissolution rate of carbon from the graphite rod into the product iron is much slower than either the diffusion rate of carbon in the iron or the reaction rate of iron oxide by carbon diffused in the iron. This results in the product iron being very low in carbon and ferritic in structure.

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