Reduction of Iron-Silicon-Oxysulfide by CO Gas Injection

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The reduction of liquid oxysulfide in the Fe-Si-S-O system by CO gas injection has been studied by monitoring the exit gas composition. The reduction rate of oxygen was calculated from the volume of evolved CO_2. Sulfur-bearing species such as COS were close to the detection limit of the mass spectrometer, which indicated that the reduction of sulfur was very limited. The volume of evolved CO_2 reached steady values 1 minute after CO injection. The reduction reaction was controlled by a chemical reaction. The observed maximum reduction rate of oxygen at 1250 °C was 8.3×10^{-6} g-O/cm^2 s, which was within the range of the reduction rates in other melts such as iron oxide and iron silicates.

I. INTRODUCTION

THE reduction of iron oxides in the temperature range below the melting point of iron appears to be a potential production route for high-purity iron. It has been reported that metallic iron is produced from Fe-S-O melts by CO gas rejection at 1200 °C,[1–4] which is lower than the melting point of iron (1535 °C). Impurities are limited because the solid solubility of impurities in metallic iron is very low at the given temperature. For example, sulfur dissolves in liquid iron over 0.1 wt pct at 1535 °C, but the solubility of sulfur in iron at 1200 °C is only 0.02 wt pct.[5] A value of 2.0×10^{-5} g-O/cm^2 s was observed to be the maximum reduction rate at 1200 °C.[3] The sulfur emissions were not a serious problem because the reduction rate of sulfur was low. The most important advantage of this oxysulfide bath is that the Fe-S-O system exhibits a liquid-phase field at a very low temperature, with a eutectic at 920 °C, permitting a low smelting temperature compared to the conventional processes. This would result into a high output per unit volume of the reactor, a low energy consumption, and the production of pure metallic iron. The present study was carried out to extend the investigation to the Fe-Si-S-O system. Very few studies of the reduction behavior in the Fe-Si-S-O system are described in the literature. The purpose of this article is to report the reduction behavior of Fe-Si-S-O melts by CO gas injection.

II. EXPERIMENTAL

The equipment used in the experimental setup consisted of a sealed furnace, which was powered by a 10 kHz, 50 kW induction generator, and a gas supply system. The matte was held in an iron crucible that was set in an alumina crucible. The alumina crucible was in a graphite crucible that acted as a suscepter for induction heating. Only the lower half of the iron crucible was filled with the matte. Injection gas was injected through an alumina tube at a rate between 8.3 and 25 cm^3/s. The gas inlet was positioned 3 cm below the melt surface only at the time of injection. This inlet was usually held about 5 cm above the melt when the injection was not performed. The gas inlet of the furnace also allowed the system to be flushed with argon during fusion of the matte and between experiments. The gas train supplied the high-purity (99.9 pct purity) CO and Ar inlet gases. The CO and Ar-CO gas mixtures ($P_{CO} = 0.5$ and 0.3 atm, respectively) were used as an injection gas. The CO gas was injected in most experiments ($P_{CO} = 1$ atm).

The matte charges were blends of commercially produced FeO, FeS, and SiO_2. The Matte composition used in this study is shown in Table I. The amount of FeO, FeS, and SiO_2 was calculated to obtain a 1 kg Fe-Si-S-O melt.

The temperature of the matte inside the coil was monitored by inserting a Pt-10 pct Rh-Pt alloy wire thermocouple inside the alumina tube. Once the desired temperature inside the coil had been reached, each matte was isothermally held for 30 minutes. During this time, Ar was flushed through the system at a flow rate of 2 L/min. The reduction reaction was studied at the temperatures of 1150 °C and 1250 °C. At these temperatures, the liquid oxysulfide melt was obtained.

After confirming that the gas composition in the furnace was pure argon, the tip of the alumina injection tube was set 3 cm below the melt surface. When the injection gas was changed from Ar to CO, a digital stopwatch was switched on. Subsequently, the exit-gas composition was analyzed by the mass spectrometer. The reduction rate was calculated from data of the exit-gas composition after CO injection.

III. RESULTS AND DISCUSSION

Before CO injection, the reactor was filled with Ar. When CO was injected at a constant flow rate, the partial pressure of Ar (P_{Ar}) decreased, and the partial pressure of CO (P_{CO}) increased with the partial pressure of CO_2 (P_{CO_2}). Monitoring the partial pressure of CO_2 gas is very important for analysis of the rate of reduction of oxygen in the Fe-Si-S-O melt. The ratio of $P_{CO_2}/(P_{CO} + P_{CO_2})$ reached steady values 1 minute after CO injection. Sulfur-bearing species such as COS, H_2S, and CS_2 were close to the detection limit of the mass spectrometer in this study. The concentrations of sulfur-bearing species to be expected in the exit gas at equilibrium for the Fe-S-O system were reported to be 8.8×10^{-5} atm for COS and 9.3×10^{-7} atm for SO_2 at 1200 °C.[2] It is to be seen also in the Fe-Si-S-O system that the principal sulfur-bearing species is COS, and the rate of removal of sulfur is less than approximately 1/1000 that for oxygen.

The ratios of $P_{CO_2}/(P_{CO} + P_{CO_2})$ in the exit gas at steady

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Table I. Matt Composition Used for This Study

Composition	Fe	Si (Wt Pct)	O	S	FeO	SiO_2 (Wt Pct)	FeS
1	59.3	9.4	24.0	7.3	60	20	20
2	60.8	9.4	26.2	3.6	70	20	10

Table II. $P_{CO2}/(P_{CO} + P_{CO2})$ in Exit Gas at Steady State

Composition	Gas Flow Rate (L/min)	P_{co} in Inlet Gas	Temperature (°C)	$P_{CO2}/(P_{CO} + P_{CO2})$ in Exit Gas
1	0.5	1.0	1150	0.039
1	0.5	1.0	1250	0.044
2	0.5	1.0	1150	0.039
2	0.5	1.0	1250	0.042
1	1.0	1.0	1150	0.032
1	1.0	1.0	1250	0.035
1	1.0	0.5	1250	0.018
1	1.0	0.3	1250	0.011
2	1.0	1.0	1150	0.032
2	1.0	1.0	1250	0.036
1	1.5	1.0	1150	0.029
1	1.5	1.0	1250	0.032
2	1.5	1.0	1150	0.030
2	1.5	1.0	1250	0.032

state are shown in Table II. The values of $P_{CO_2}/(P_{CO} + P_{CO_2})$ for the Fe-Si-S-O melt, for compositions 1 and 2, ranged from 0.011 to 0.044. Higher values were obtained at 1250 °C. The values of $P_{CO_2}/(P_{CO} + P_{CO_2})$ were dependent on the P_{CO} in the inlet gas at the flow rate of 1.0 L/min. This means that the reduction rate of oxygen is a function of P_{CO} in the inlet gas.

When the oxygen in oxysulfide melts ([O]) is reacted with CO gas, the following reduction reaction can be written:

$$[O] + CO\ (g) = CO_2\ (g) \qquad [1]$$

The reduction rate of oxygen can be calculated from the volume of evolved CO_2. The following mass balance of CO_2 and Ar can be written for the reduction reaction:

$$W\ (dn^r_{CO_2}/dt) = v\ (-n^{out}_{CO_2} + n^{in}_{CO_2}) + A\ W\ r_o/16 \qquad [2]$$

$$W\ (dn^r_{ar}/dt) = v\ (-n^{out}_{Ar}) \qquad [3]$$

where n^r_i is the mole value of species i in the reactor, n^{out}_i is the mole value of species i in the exit gas, n^{in}_i is the moles of species i in the inlet gas, r_o is the reduction rate of oxygen (in g-O/cm^2 s), W is the volume of reactor (in cm^3), v is the gas flow rate (in cm^3/s), and A is the reaction surface area (in cm^2).

According to the definition of reactors by Levenspiel,[6] the reactor in this study corresponds to a mixed-flow reactor. It is a reactor in which the contents are well mixed by stirring and are uniform in composition throughout.

When the reactor is assumed to be the mixed-flow reactor,

$$n^r_i = n^{out}_i \qquad [4]$$

Rearranging the previous equations in terms of the partial pressure,

$$W\ (dP^{out}_{CO_2}/dt) = v\ (-P^{out}_{CO_2} + P^{in}_{CO_2}) + ART\ r_0/16 \qquad [5]$$

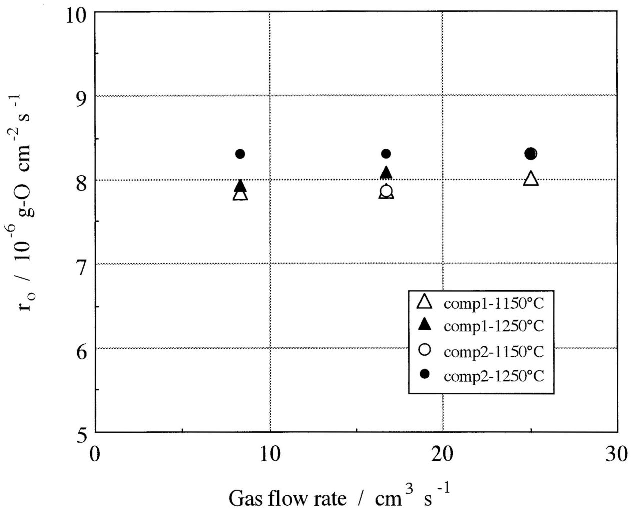

Fig. 1—Effect of gas flow rate on the reduction rate of oxygen.

$$W(d\ P^{out}_{Ar}/dt) = v\ (-P^{out}_{Ar}) \qquad [6]$$

The reduction rate of oxygen was calculated based on Eq. [5] in this study. Integrating Eq. [6] by using the initial condition that P_{Ar} ($t = 0$) is 1 atm,

$$\ln P_{Ar} = -(W/v)t \qquad [7]$$

The measured data of P_{Ar} and time confirm this relationship. The volume of the reactor was calculated to be 5.6×10^3 cm^3. This value was close to the actual volume of the reactor.

The area of the reaction surface was calculated from the sum of the surface area of the bubbles, as studied before.[3] The bubble diameter could be estimated by equations known in fluid dynamics.[7] The rate of generation of the surface area of the bubbles (A_b) is given by

$$A_b = 1.56\ v^{0.71}\ \text{cm}^2/\text{s} \qquad [8]$$

The generation rate of the surface area of the bubbles increases with increasing gas flow rates. The value of A_b was used for the calculation of the total surface area per second.

The effect of CO gas flow rate on the reduction rate of oxygen from the oxysulfide melt is shown in Figure 1. The reduction rate also becomes constant in 1 minute. At high gas flow rates, the time to reach the constant reduction rate is shortened and the calculation of the reduction rate becomes much simpler at this steady state of reduction. The reduction rate for the melt of composition 2 is 8.31×10^{-6} g-O/cm^2 s at 1250 °C. This is the maximum observed value of the reduction rate of oxygen from an oxysulfide melt by CO gas injection.

The reaction mechanisms for the reduction can be subdivided into kinetic and reaction steps, such as mass-transfer control in the gas phase, mass-transfer control in the liquid phase, and chemical-reaction control on the reduction of oxygen. A selected step in a proposed reaction mechanism can be assigned a rate expression that would be observed if all previous and subsequent steps in the mechanisms are fast and virtually at equilibrium. It would be important and interesting to determine which of the steps could be controlling the overall reaction rate.

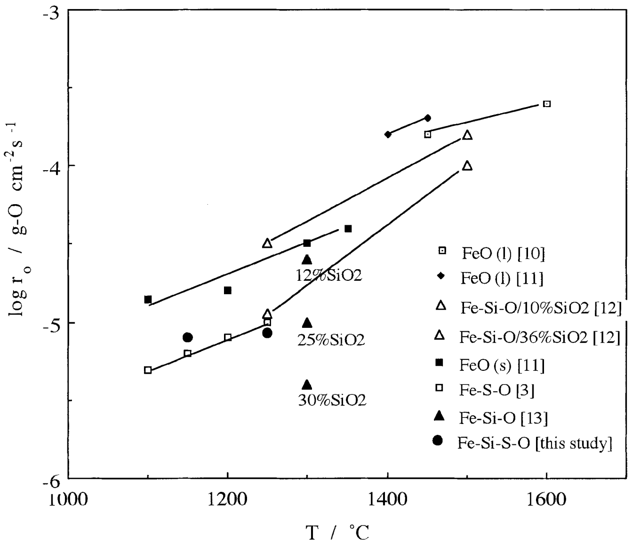

Fig. 2—Reduction rate of oxygen. $P_{CO} = 1$ atm.

When the chemical reaction is very fast, the concentration of gas is low, or the mass-transfer coefficient of the gas is low, gas-phase mass-transfer control would be expected. But it would not be the controlling step in this study, because the reduction rate of oxygen was independent of gas flow rates.

Under liquid-phase mass-transfer control, the observed reaction rate is dependent on the difference between the activity of oxygen at the surface of the melt and that of the bulk liquid, which may apply when CO gas is blown to the surface of the melt. From the following empirical relationship,[8] the required mixing time (t_m) for the injected oxysulfide melt was calculated to be about 10 seconds.

$$t_m = k \{(M/\rho)^{2/3} \varepsilon^{-1}\}^{1/3} \qquad [9]$$

where k is a constant, M is the weight of the liquid, ρ is the density of the liquid, and ε is the stirring work per unit weight of metal. The reduction rate of oxygen was a function of P_{CO} in the injecting gas. These suggest that the mass transfer in the liquid phase is not likely to be a controlling step.

It was shown that the reduction rate of oxygen was independent of gas flow rates, which supports the assumption that the reduction of oxygen in this study is controlled by a chemical reaction.

The ionic behavior of the species is also possible for the Fe-O-S melts.[9] Equation [1] can be rewritten as

$$[Fe^{2+}] + [O^{2-}] + CO\ (g) = Fe\ (s) + CO_2\ (g) \qquad [10]$$

But the ionic behavior of silicon species such as Si^{4+} and SiO^{2+} is not well known in the Fe-Si-S-O system. The overall reduction rate of Eq. [1] is

$$r_0 = k_f a_O P_{CO} - k_b P_{CO_2} \qquad [11]$$

where k_f and k_b are reaction-rate constants for the forward and reverse reactions, respectively. Substituting the ratio of k_f to k_b (K),

$$r_0 = k_b P_{CO}\ (K\ a_0 - P_{CO_2}/P_{CO}) \qquad [12]$$

An Arrhenius plot of the reduction rates of various ferruginous melts by gas is shown in Figure 2. There are few studies on the reduction of iron-silicon-oxysulfide melts. On the other hand, studies on the reduction from iron oxide–bearing slags have been carried out by many investigators.[3,10–13] The observed values in this study were of the same order of reduction rate for Fe-Si-O melts.[12,13] For silicate slags containing up to 68 pct FeO, 12.4 pct SiO_2, 14.2 pct CaO, and 5.7 pct MgO, the rate of reduction was independent of FeO content down to 48 pct, with a rate constant of 3.3×10^{-4} g-O/cm^2 s at 1600 °C.[14] The reduction rates of oxygen in this study were within the range of the reduction rates in other melts such as iron oxide or iron silicates.

IV. CONCLUSIONS

The reduction behavior of Fe-Si-S-O melts by CO gas injection was studied at 1150 °C and 1250 °C. The reduction reaction was controlled by a chemical reaction between the oxygen in the melt and the CO gas. The sulfur emissions were very low. The observed maximum reduction rate of oxygen at 1250 °C was 8.3×10^{-6} g-O/cm^2 s, which was within the range of the reduction rates in other melts such as iron oxide and iron silicates.

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