Effect of Gas Composition on the Carbothermic Reduction of Manganese Oxide

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This paper examines the reduction of pure MnO, Groote Eylandt (Northern Australia) manganese ore, siliceous manganese fines and ferromanganese slag by graphite. Reduction was conducted in the stagnant atmosphere of argon, Ar–CO gas of varying composition and helium. The rate and extent of reduction were determined by thermo-gravimetric analysis and by monitoring CO and CO₂ concentrations in the gas phase. The rate of MnO reduction in Ar–CO gas increased with decreasing CO partial pressure. Reduction in helium was faster than in argon. Under given experimental conditions (stagnant gas atmosphere) the reduction rate was mix-controlled by CO mass transfer in the gas phase and chemical reaction.

KEY WORDS: manganese; carbothermic reduction; argon, carbon monoxide; helium; kinetics.

1. Introduction

Manganese ore upon melting consists of two phases: solid MnO-phase, which may be a pure MnO oxide or MnO–MgO solid solution, and liquid oxide phase referred to as a slag phase. The process of manganese ore reduction includes MnO-phase dissolution into the molten slag and MnO reduction from the slag.1–4)

MnO reduction by graphite or carbon dissolved in metal is presented by the following reaction:

\[(\text{MnO}) + \text{C} \rightarrow [\text{Mn}] + \text{CO}\]

The overall reduction reaction includes the following steps: 1) dissolution of solid MnO phase into the molten “slag” phase in the reduction of manganese ore and siliceous manganese fines, 2) liquid phase mass transfer of MnO, 3) dissolution of carbon into the metal phase, 4) carbon mass transfer in liquid metal, 5) carbon-oxide chemical reaction (intrinsic control), and 6) CO mass transfer from the reaction interface to the gas phase.

The resistance due to carbon dissolution and diffusion in liquid metal is usually considered negligible. Resistance due to MnO transfer in the molten slag can contribute to the rate control,5) although literature data on this matter are controversial. In accordance with work,6) slag stirring in the carbothermic ferromanganese slag reduction had no effect on the reduction rate, what means that resistance due to the mass-transfer in the slag phase may be neglected. This was also concluded by Tangstad on the basis of analysis of the MnO concentration profile in the slag. The intrinsic control of the MnO reduction is widely accepted in literature.

The resistance due to CO mass transfer in gas phase can also contribute to the reduction kinetics. In accordance with Refs. 1), 7) manganese ore reduction is retarded by increasing CO partial pressure. Data obtained by Terayama and Ikeda on carbothermic MnO reduction in helium show that MnO is reduced much faster in helium than in argon, what can be related to different diffusion coefficients of CO in helium and argon.

Effect of gas atmosphere on MnO reduction is examined in this paper, which presents results on reduction of pure MnO, Groote Eylandt manganese ore, siliceous manganese fines and ferromanganese slag by graphite in argon, Ar–CO gas of varying composition and helium. Effect of chemistry of manganese-containing materials on the MnO reduction rate was discussed elsewhere.1,4)

2. Experimental

Reduction of pure MnO, manganese ore and ferromanganese slag was investigated using thermogravimetric analysis (TGA) coupled with CO and CO₂ analysis in the off gas.

Experimental set-up and procedure were described in detail elsewhere.1) The gas atmosphere was made from high purity Ar, CO and He cleaned of water, oxygen and CO₂. The flow rate of gases and gas composition were controlled using mass flow controllers. The total gas flow rate was maintained at 1.6 l/min. The inert gas, or Ar–CO gas mixture was introduced to the TGA from its bottom and was withdrawn from the top, bypassing the crucible containing a sample. Such experimental arrangement made the gas atmosphere within the crucible stagnant. The exit gas was continuously sampled at a rate of about 0.1 l/min and directed to an infrared CO/CO₂ analyser. Graphite crucibles were of near cylindrical shape with dimensions 17 mm OD, 11 mm ID and 24 mm height. A sample mass was of 0.5 g.

Compositions of manganese ore, siliceous manganese...
fines and ferromanganese slags examined in this paper are given in Table 1. The ores were sized between 50 and 150 μm and calcined at 1 000°C under Ar prior to reduction experiments. Size of slag samples was in the ranges of 75–90 and 500–600 μm. Reduction was investigated in the temperature range of 1 000–1 450°C for pure MnO and manganese ores, and 1 300–1 550°C for ferromanganese slags.

The extent of reduction was measured by recording the mass loss and concentration of CO in the exit gas in the course of reduction. The discrepancy between the weight loss data and CO evolution was mainly attributed to vaporisation of manganese, although reduction of SiO2 to the gaseous SiO and reduction of Na2O and K2O with formation of Na and K vapour also contributed to the measured weight loss. Concentration of CO2 in the exit gas was negligible.

### Table 1. Compositions of manganese ores and ferromanganese slags, wt%.

|                  | Initial ore 1 | Calced ore | Calced siliceous manganese fines | FeMn slag 1 | FeMn slag 2 |
|------------------|--------------|-----------|---------------------------------|-------------|------------|
| Mn(4)            | 51.2         | 20.3      |                                 | MnO         | 35.5       |
| Mn(total)        | 53.3         | 61.1      | 44.69                           | SiO2        | 25.5       |
| SiO2             | 2.60         | 3.04      | 12.84                           | Al2O3       | 15.6       |
| Fe(2)            | 0.31         | <0.05     |                                 | CaO         | 13.6       |
| Fe(3)            | 2.84         | 3.56      |                                 | BaO         | 2.64       |
| Fe(total)        | 3.15         | 3.56      | 10.95                           | K2O         | 3.21       |
| Al2O3            | 2.40         | 2.81      | 9.74                            | MgO         | 1.52       |
| BaO              | 2.29         | 2.68      | 0.86                            | TiO2        | 0.66       |
| K2O              | 0.70         | 0.82      | 1.202                           | Na2O        | 0.55       |
| SrO              | 0.17         | 0.20      | 0.06                            | S           | 0.40       |
| TiO2             | 0.15         | 0.18      | 0.46                            | FeO         | 0.28       |
| CaO              | 0.08         | 0.09      | 0.19                            | SrO         | 0.26       |
| PbO              | 0.07         | 0.08      | 0.16                            | Fe2O4       | 0.10       |
| Na2O             | 0.44         |           | 0.05                            | ZrO2        | 0.05       |
| P2O5             |              |           | 0.01                            | P2O5        | 0.03       |

3. Results

3.1. Pure MnO Reduction

TGA data on the MnO mass loss in the reduction experiment at 1 300°C under CO–Ar gas of varied composition are presented in Fig. 1. In this experiment, concentration of CO in the CO–Ar gas decreased from 100 to 35 vol%, then increased to 45 vol%, and switched to 100 vol% CO afterwards. Addition of CO to argon strongly retarded MnO reduction. At this temperature, reduction started when CO content was below 75 vol% and proceeded at a reasonable rate only when CO content was below 35–45 vol%. The switch of the gas atmosphere to 100 vol% CO caused partial reoxidation of manganese.

In the non-isothermal experiment presented in Fig. 2, reduction of pure MnO by graphite under CO atmosphere started at 1 320°C. Reduction of MnO by solid carbon in a CO atmosphere was much slower than that under argon. Effect of CO–Ar gas composition on MnO reduction decreased with increasing temperature.

TGA data, and CO and CO2 evolution curves in the reduction experiment at 1 350°C in helium and in argon are plotted in Fig. 3. The rate of MnO reduction was notably faster under helium.

3.2. Reduction of Manganese Ore

Reduction of manganese ore under CO in comparison with that under argon at 1 300°C and 1 350°C is depicted in...
Reduction of manganese ore in the CO atmosphere was much slower than in argon, particularly at the lower temperature of 1300°C. The initial stage of reduction, at which iron oxides were reduced to metallic iron and higher manganese oxides to MnO, was not notably affected. The retarding effect of CO was exhibited in the second reduction stage, at which MnO was reduced to the metallic phase. In some experiments performed at 1300°C, the original CO atmosphere was switched to argon, or the original argon atmosphere was switched to CO. The switch of CO to Ar strongly accelerated the reduction process (Fig. 4). The switch of Ar to CO atmosphere caused some re-oxidation of a sample. The reoxidation of manganese carbide was much slower than reduction of MnO, possibly, due to the passivation. The reoxidation, practically, stopped after achieving degree of reaction of about 10%.

Reduction of manganese ore under helium was examined at 1400°C. The reduction curves, obtained under helium and argon, were close to each other; manganese ore was reduced slightly faster in helium than in argon (Fig. 5).

3.3. Reduction of Siliceous Manganese Fines

Effect of CO–Ar gas composition on the extent and rate of reduction of siliceous manganese fines was examined at 1350°C. Results are presented in Fig. 6. Increase in CO concentration in the CO–Ar gas mixture strongly retarded the rate of reduction. The first stage, in which manganese oxides were reduced to MnO and iron oxides to metallic iron, was practically unaffected and it was the second stage, at which MnO was reduced to metallic phase, that bore the impact. The slope of the TGA curve at the second reduction stage in carbon monoxide was about half of that obtained in argon.

TGA-reduction curves for siliceous manganese fines in argon and helium at 1350°C are compared in Fig. 7. Reduction of siliceous fines in helium proceeded faster than in argon. The difference in the rate of reduction when conducted under a helium atmosphere to that under an argon atmosphere was obviously greater than in the case of the standard manganese ore.

3.4. Reduction of Ferromanganese Slag

Effect of CO–Ar gas composition on the extent and rate of reduction of ferromanganese slags was examined at 1400°C. The introduction of CO into the Ar atmosphere resulted in a dramatic decrease in both rate and extent of reduction (Figs. 8 and 9). The very beginning of the FeMn reduction was not affected by the CO–Ar gas composition but past this stage there was a very strong influence. After one hour, reduction of FeMn slag by graphite in CO atmosphere achieved only about 1/3 of the reduction extent of that in argon.

Changing the argon gas atmosphere to helium also had a strong effect on the reduction of FeMn slag. Both TGA and CO evolution data showed that the rate of FeMn slag reduction by graphite under He was much faster than that experienced under argon (Fig. 10). The effect of changing the gas
faster in helium than in argon. This gives a basis to conclude that under experimental conditions employed in this work (stagnant gas atmosphere in the crucible), MnO reduction was mix-controlled by chemical reaction and CO mass transfer in gas phase.

The rate of the chemical reaction is

\[ R = k_A (\alpha_{MnO} - P_{CO}^a \alpha_{Mn}^a / K) \] .......................... (1)

where \( k \) is the rate constant, \( A \) is the reaction interfacial area, \( \alpha_{MnO} \) is MnO activity in the molten slag, \( P_{CO}^a \) is CO partial pressure at the reaction interface, \( \alpha_{Mn}^a \) is manganese activity in the metallic phase and \( K \) is the equilibrium constant of the reduction reaction.

CO mass transfer from the reaction interface to the bulk gas, actually, consists of two steps: 1) CO evolution in the melt (as discussed in Section 3), and 2) CO mass transfer from the melt to the bulk gas. The first step should not depend on the gas composition. However, a "bath" was formed in the experiments. Graphite-ore system formed a solid-liquid mixture in which the reaction interface could be exposed to the gas phase. It is assumed that CO partial pressure at the reaction interface is equal to CO partial pressure on the sample surface: \( P_{CO}^i = P_{CO}^a \).

The rate of CO mass transfer from the sample surface through the stagnant gas atmosphere in the crucible to the bulk gas may be presented as:

\[ N_{CO} = A_d D 10^{5/3} (RT \delta)(P_{CO}^i - P_{CO}^b) = \beta A_d (P_{CO}^a - P_{CO}^b) \] .......................... (2)

Where \( D \) is the CO diffusivity in the gas phase, \( m^2 \cdot s^{-1} \), \( \delta \) is the diffusion layer thickness, \( m \), \( A_d \) is the area for gas diffusion, \( m^2 \), \( P_{CO}^i \) and \( P_{CO}^a \) are CO partial pressures at the reaction interface and the sample surface respectively; \( \beta = D 10^{5/3} (RT \delta) \) is efficient mass transfer coefficient in mol \( \cdot m^{-2} \cdot s^{-1} \cdot atm^{-1} \).

Equation (3) for the MnO reduction rate is derived by manipulating with Eqs. (1) and (2) (steady state conditions):

\[ R = k \beta A_d \alpha_M (\alpha_{MnO} - P_{CO}^a \alpha_{Mn}^a / K) / (\beta A_d + k \alpha_M) \alpha_M / K) \] .......................... (3)

This equation is used to assess the thickness of the gas boundary layer and chemical reaction rate constant.

Let us consider the manganese ore reduction in argon and helium under otherwise the same experimental conditions: temperature, CO partial pressure in the bulk gas (assumed to be zero), ore and graphite size, and assume that the boundary layer thickness is the same. Then, the reduction rates in argon and helium are presented by Eqs. (4) and (5) correspondingly.

\[ R_A = k \beta A_d \alpha_M (\alpha_{MnO} - P_{CO}^a \alpha_{Mn}^a / K) / (\beta A_d + k \alpha_M) \alpha_M / K) \] .......................... (4)

\[ R_H = k \beta A_d \alpha_M (\alpha_{MnO} - P_{CO}^a \alpha_{Mn}^a / K) / (\beta A_d + k \alpha_M) \alpha_M / K) \] .......................... (5)

where \( k^* = k \beta A_d \alpha_M (\alpha_{MnO} - P_{CO}^a \alpha_{Mn}^a / K) / (\beta A_d + k \alpha_M) \alpha_M / K) \) and \( D_A \) and \( D_H \) are CO diffusion coefficients of MnO in argon and helium.

The ratio of the reduction rates in argon and helium is:

\[ R_A / R_H = D_A (D_A 10^{5/3} (RT)A_d + \zeta) / (D_H 10^{5/3} (RT)A_d + \zeta) \] .......................... (6)

Experimentally measured ratio \( R_A / R_H \) for reduction of MnO from ferromanganese slag at 1 400°C is equal to 0.46.

4. Discussion

The rate of carbothermic reduction of pure manganese oxide, MnO from manganese ore, siliceous manganese fines and from ferromanganese slag was strongly affected by the gas composition. Introduction of CO to argon retarded the reduction process; reduction of manganese oxide was particularly dramatic at the beginning of reduction.
CO diffusion coefficients in argon and helium at 1400°C were calculated using Fuller, Schettler and Giddings equation\(^9\): 

\[
D_{\text{Ar}} = 3.60 \times 10^{-4} \text{ m}^2/\text{s}, \quad D_{\text{He}} = 16.9 \times 10^{-4} \text{ m}^2/\text{s}
\]

The exposed surface area of a sample to the open atmosphere was \(1.84 \times 10^{-4} \text{ m}^2\). Using these data, parameter \(\zeta\) is found to be \(5.34 \times 10^{-7}\).

Experimental value of \(R\) for the ferromanganese slag reduction in argon at 1400°C is: 

\[
R_{\text{Ar}} = 2.4 \times 10^{-6} \text{ mole CO} \cdot \text{s}^{-1} \cdot \text{m}\] ^2
\]

MnO activity in the ferromanganese slag in the beginning of reduction is 0.4 (see Ref. 10)). The effective chemical reaction rate constant \(k^*\) calculated using Eq. (4) is \(5.5 \times 10^{-5} \text{ mol} \cdot \text{m}^2 \cdot \text{s}^{-1}\).

Then, using \(\zeta = k^* a_{\text{Mn(MnO)}} / K = 5.34 \times 10^{-7}\), manganese activity in the Mn–C\(_{\text{sat}}\) solution \(a_{\text{Mn}} = 0.41\), \(k^* = 5.5 \times 10^{-5} \text{ mol} \cdot \text{s}^{-1}\) and equilibrium constant, \(K_{1400^\circ\mathrm{C}} = 0.796\), the diffusion thickness layer \(d\) is found equal to 0.017 m.

Under given experimental conditions, the stagnant layer of about 1.5 cm extended from the sample surface to the crucible top. Therefore, a boundary layer thickness of 1.7 cm is not unreasonable.

The main constraint in this approach is uncertainty in determination of interfacial area for the chemical reaction and gas/sample area.

5. Conclusion

Carbothermic reduction of pure MnO, manganese ore and ferromanganese slag is strongly affected by the gas composition. Introduction of CO to argon retarded the reduction process; reduction of manganese oxide was faster in helium that in argon. Under experimental conditions employed in this work, the reduction rate was mix-controlled by interfacial chemical reaction and CO mass transfer in the gas phase.

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Nomenclature

- \(A_c\): Interfacial area for reduction reaction (m\(^2\))
- \(A_d\): Crucible cross-sectional area (m\(^2\))
- \(a_{\text{Mn(MnO)}}\): Thermodynamic activity of Mn or MnO
- \(D\): Diffusion coefficient in the gas phase (m\(^2\) s\(^{-1}\))
- \(K\): Equilibrium constant
- \(k^*\): Chemical reaction rate constant (mol \cdot m\(^2\) s\(^{-1}\))
- \(k^* = k_A\)
- \(P_{\text{CO}}^s\): Partial pressures of CO at the sample surface (atm)
- \(P_{\text{CO}}^b\): Partial pressures of CO in the bulk gas (atm)
- \(R\): Reaction rate (mol \cdot s\(^{-1}\))
- \(\beta = D10^{3/(RT\delta)}\)
- \(\delta\): Diffusion layer thickness (m)
- \(\zeta = k^* a_{\text{Mn}} / K\)

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