Carbothermic Reduction of Manganese from Manganese Ore and Ferromanganese Slag

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Abstract

The carbothermic reduction of Australian Groote Eylandt manganese ore and TEMCO ferro-manganese slag was studied thermogravimetrically. Samples were prepared by intimately mixing calcined manganese ore or slag and graphite. Experiments were performed using graphite crucibles at temperatures ranging from 1000°C to 1550°C under Ar-CO gas atmospheres. In a number of experiments, concentrations of CO and CO_2 in the off-gas were monitored using infra-red analysis. Samples reduced to different extents were examined using a FESEM, electron microprobe and optical microscopy. Data on the rate of reduction and phase composition were used to elucidate the reduction mechanisms. Rate and extent of the manganese ore reduction increase with increasing temperature. Silica has a strong retarding effect on the rate of manganese reduction. Addition of CO to the argon atmosphere markedly decreases the rate of ferromanganese slag reduction, but has a less retarding effect on the rate of manganese ore reduction.

Introduction

Pure MnO reduction has been suggested to occur via CO gas, with the rate controlled by the Boudouard reaction [1), 2), 3), 4)]. The rate of the Boudouard reaction has been suggested to be limited by CO_2 mass transfer from the reaction interface to solid carbon.

Two different mechanisms have been proposed for the reduction of manganese ore

1. Reduction of manganese ore through direct contact of the oxide phase with carbon containing phase resulting in the formation of a metal-carbide phase.[5), 4), 6), 7), 8), 9)] This reaction has been suggested, to be controlled by the chemical reaction between the oxide and carbon [6)], or by MnO mass-transfer through the oxide phase. [10), 4)]

2. Reduction of manganese ore by CO with CO regenerated by the Boudouard reaction. The rate of this reaction is suggested to be limited by the Boudouard reaction. [10), 4)]

Tangstag and Olsen [9)] in their study of reduction of BHP (Groote Elyandt) manganese ore, have found that two oxide phases coexist at temperatures of 1335°C, which are a slag phase and a solid MnO phase. These two phases were also observed by Ostrovski and Webb [5)] in the reduction of siliceous manganese ore at 1000, 1200 and 1400°C. Increase in the silica content decreases the solid MnO phase to slag ratio, and MnO activity coefficient in the slag. [9)]

The reduction of MnO from silicate slag was investigated by Skjervheim and Olsen [11)] in a segregated phase bath system (in contrast to the current dispersed powder arrangement). Their findings concluded, that the rate of reduction of manganese and silicon is chemically controlled and that lowering the CO partial pressure enhances the rate of reduction.

The extent and kinetics of manganese ore reduction strongly depend on the ore composition. Thus, results obtained by Ostrovski and Webb[5)] for the reduction of Australian Groote Eylandt siliceous manganese fines differed significantly from the results of Eric and Burucu [4)] for lower silica South African Mamatwan manganese ore.

Manganese reduction from siliceous manganese fines[5)] was found to occur predominantly by the carbon of the carbide phases, initially formed as a result of iron reduction. Metallic iron nucleation in the first stage of reduction was rather uniform in the manganese ore interior. Reduction of manganese into the metallic state and its concentration were predominantly observed in the metallic spots in the contact with graphite particles, indicating that manganese was reduced by carbon of the metallic phases, which in turn, was supplied by graphite through direct contact. The limiting step of this process was suggested to be manganese diffusion in the slag phases.

Thus, survey of the literature shows that manganese may be reduced from its ore, FeMn-slag, and pure MnO by different mechanisms. These mechanisms, which depend on the material chemistry and physical conditions, are generally not well understood. The aim of the current work was to establish the mechanisms prevailing in the carbothermic reduction of manganese from manganese ore and FeMn slag.

Experimental

The extent and rate of reduction was investigated using thermogravimetric analysis (TGA) coupled with CO and CO_2 analysis (figure 1). A Ceramic Engineering molybdenum di-silicide electric furnace controlled by an Eurotherm controller, provided a maximum sample temperature of 1650°C. This furnace was

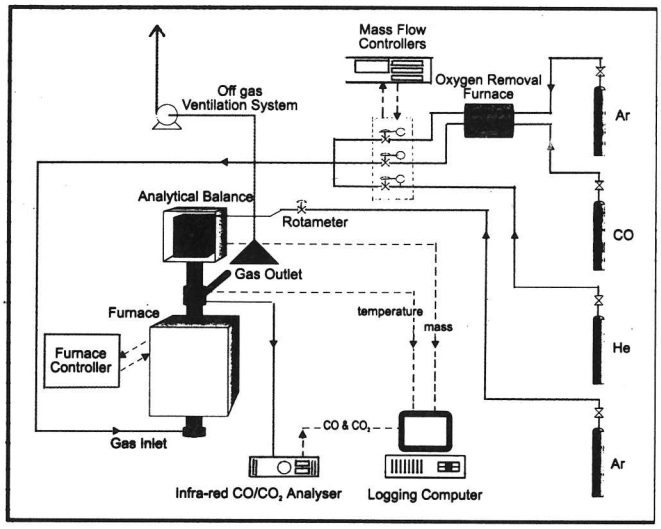

Fig. 1. Experimental TGA equipment

electrically moved up and down to achieve controlled insertion and withdrawal of the sample. The sample was suspended from a Precisa 180 balance (180g maximum with +/-.0001g accuracy) using a stainless steel wire followed by a molybdenum wire. The gases supplied were high purity Ar and CO cleaned of water and CO_2 by an Alltech Hydro- Purge II and oxygen by passing over titanium sponge at 600°C. The flow rate of gases to the apparatus was primarily controlled using Brooks mass flow controllers and occasionally a Brooks Sho-Rate rotameter. Purging was accomplished in two stages, first 10minutes at 30L/min through the balance chamber followed by 10 minutes at the same flow rate flow rate was 1.6L/min. The exit gases were continuously sampled at a rate of about 0.5 L/min from within the top end of the working tube and fed through a Hartmann and Braun infra-red CO/CO_2 analyser.

Typical crucibles used were 24mm tall, 17mm top outer diameter and 11mm top inner diameter tapered down at an angle of 7°. Samples were generally 0.5g, being a mixture of oxide (100μm) and graphite (98%C, 100μm) consisting of 30% excess carbon to oxide for the reduction of manganese to its carbide, Mn_7C_3. The ore and FeMn-slag were supplied by BHP TEMCO, their chemical analyses are shown in table 1.

Table 1. Composition of Mn-ore and FeMn-slag (wt%)

Component	Initial	Calcined	Component	FeMn slag
Mn(4)	51.2	20.3	*MnO*	35.5
Mn(total)	53.3	61.1	*SiO_2*	25.5
SiO_2	2.60	3.04	*Al_2O_3*	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	*K_2O*	3.21
Al_2O_3	2.40	2.81	*MgO*	1.52
BaO	2.29	2.68	*TiO_2*	0.66
K_2O	0.70	0.82	*Na_2O*	0.55
SrO	0.17	0.20	*S*	0.40
TiO_2	0.15	0.18	*FeO*	0.28
CaO	0.08	0.09	*SrO*	0.26
P	0.07	0.08	*CeO_2*	0.10
			ZrO_2	0.05
			P_2O_5	0.01

The chemical composition of the graphite used is given in table 2.

Table 2. Graphite composition (wt%)

Component	wt%
Fixed	95.4
Volatile	0.6
Ash	4.0
Ash	
MnO	0.25
Fe_2O_3	10.0
SiO_2	38.25
Al_2O_3	5.75
BaO	<0.05
CaO	12.25
Na_2O	18.25
K_2O	10.5
MgO	1.25
TiO_2	0.75
P_2O_5	0.25

Weight and temperature, and CO and CO_2 analysis data were logged using LabWindows/CVI software. The time taken for insertion of the sample into the furnace was 40 seconds followed by the targeted sample temperature being achieved within approximately 1 minute.

The rates of reduction were quantified in terms of the rate of mass loss as well as CO evolution. Weight loss was due to the following factors (the first two dominating):
i) carbothermic reduction of oxides (primarily Mn and Si)
ii) vaporisation of manganese
iii) partial oxidation of the graphite crucible by trace oxygen
iv) possible reduction of SiO_2 to the gaseous SiO and reduction and vaporisation of Na_2O and K_2O.

Oxidation of the graphite crucible resulted in the production of CO_2. The production of CO was solely attributable to the reduction reaction. The difference in mass loss logged by the TGA and calculated on the basis of CO evolution was attributed to manganese vaporisation.

Raw materials were sized and calcined for 1 hr at 1000°C under argon to remove volatiles and decompose compounds such as carbonates. This also altered the oxidation state of the manganese. This procedure was undertaken to ensure that experimental loss was solely due to the reduction phenomena.

Samples were examined using optical microscopy followed by electron microscopy. Both optical and back scattered electron imaging as well as point analysis were performed using a CAMECA SX-50 electron micro-probe (15kV and 20nA). Back scattered electron images were obtained using a Field Emission Scanning Electron Microscope (Hitachi 4500 FESEM). Samples were mounted into epoxy resin disks, hand polished and coated with copper. Appropriate standards were made in parallel with the samples.

Results

Rate and extent of reduction

Experimental TGA data for manganese ore and ferromanganese slag reduction by graphite at 1000 to 1400°C under an Ar

atmosphere are presented in Fig. 2 and Fig. 3 respectively (per 1g of ore or slag).

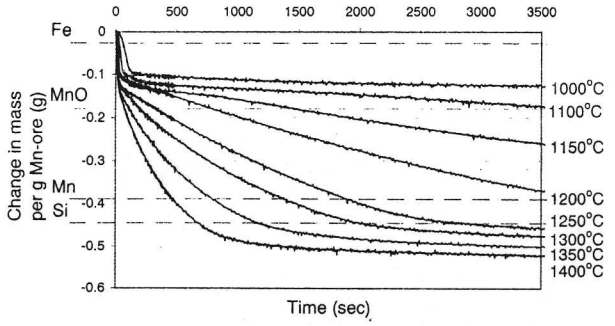

Fig. 2. Mass-loss in the process of manganese ore reduction by graphite under argon as a function of temperature.

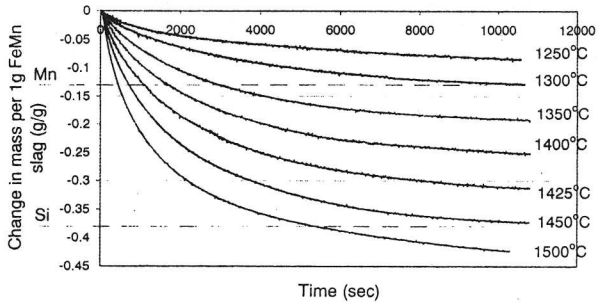

Fig. 3. Mass-loss in the process of FeMn slag reduction by graphite under argon as a function of temperature.

Calculated theoretical mass losses based on the ore composition for the reduction to iron, MnO, Mn and Si are also shown in figure 2 and those corresponding to Mn and Si in figure 3. The extension of TGA curves below the theoretical limits for complete reduction is accounted for by the vaporisation of manganese.

Infra-red analysis of the off-gas for CO and CO_2, has shown that CO_2 contents in the off-gas is negligible except in the very early moments of reduction. Carbon monoxide contents of the reaction gas is presented together with the mass change as determined by TGA, in figure 4.

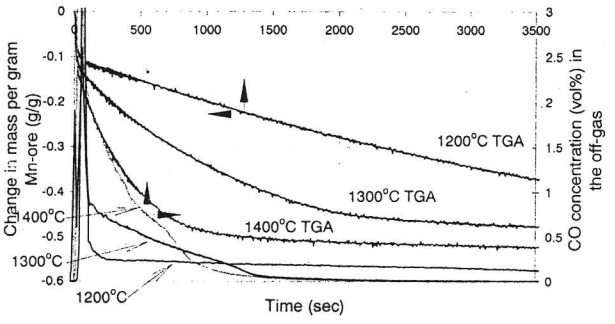

Fig. 4.TGA and CO concentration data for reduction of Mn-ore by graphite under argon.

The contribution of manganese vaporisation is clearly demonstrated: there continues to be a weight decrease even after the reaction has finished (as indicated by the cessation of CO evolution).

Reduction of manganese oxide is strongly affected by the Ar-CO gas composition. This is illustrated by figure 5, in which mass loss of the MnO-graphite mixture is plotted as a function of time for varying CO concentrations at 1300°C.

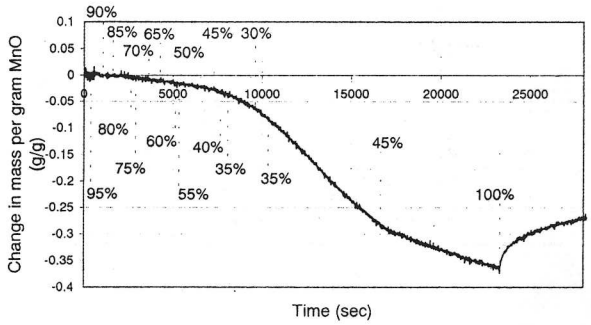

Fig. 5. MnO reduction by graphite at 1300°C under an Ar-CO atmosphere with different CO concentrations (vol%)

As follows from this figure, at 1300°C pure manganese oxide reduction starts when the CO content of the gas is less than about 70vol%. Pure MnO reduces to the metal phase in the presence of carbon in a CO atmosphere at temperatures above about 1320°C (fig. 6).

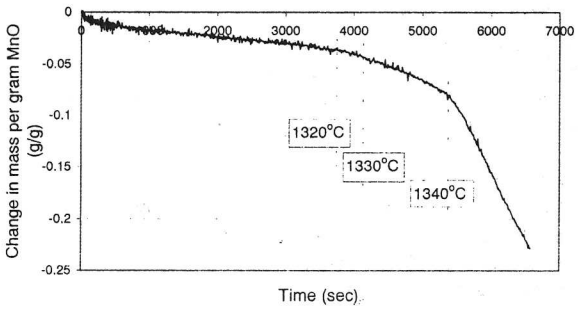

Fig. 6. MnO reduction by graphite under CO atmosphere at different temperatures.

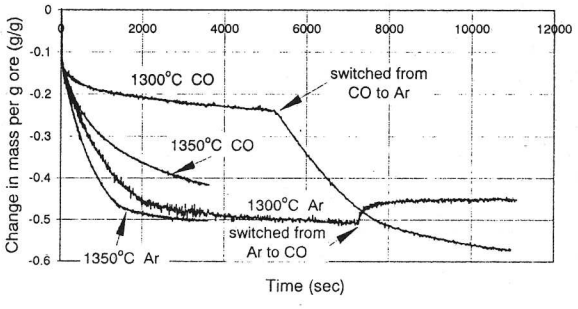

Fig. 7. Effect of CO on the reduction of Mn ore by graphite.

Reduction of MnO by solid carbon in a CO atmosphere at temperatures close to 1320°C is much slower than under argon. At

temperatures of 1350°C gas composition has less dramatic effect on the MnO reduction than at 1300°C (fig 7).

Phase analysis

Unreduced Mn-ore and selected samples taken during the reduction experiments were examined by optical and microprobe analyses.

Raw Groote Eylant manganese ore generally exhibits a banded structure as illustrated in figure 8.

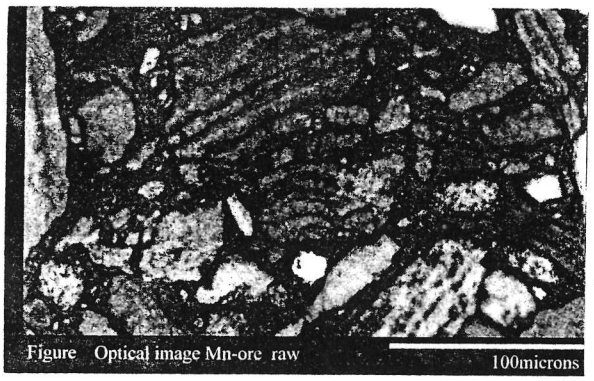

Fig. 8. Optical image of raw Manganese ore.

Analysis showed that the manganese predominantly existed in the Mn^{4+} oxidation state. After calcination at 1000°C for one hour under argon the banded structure disappeared and is replaced by two phases (white and dark). After further heating of the calcined ore at 1200°C for 90 minutes the two phase structure remained and became more distinct. Sintering also commenced at this temperature. Analysis of the phases indicated that the dark phase contained manganese in the form of MnO_2, while the white phase consisted of approximately 31wt% Mn, 53wt% O and included Si, Al and other ore components.

At 1000°C, the reduction of higher oxides of manganese to MnO, and iron to its metallic state, occurred. Reduction of manganese oxides to MnO is rather fast. Iron was seen to be nucleated into a metallic phase after about 85min, which occurred in a random fashion both in the interior of the ore and on the interfaces exposed to graphite. At 1200°C, the iron present was fully reduced into a metallic phase after only 15 minutes. The sample taken at this stage of reduction contained a light grey oxide phase, which had a low manganese content. Large metallic phases were found adjacent to the oxides, while smaller size metallic phases were located both adjacent to and within the oxide phases. Only a small portion of manganese had been reduced during this early stage of reduction.

Reduction significantly progressed with further exposure at 1200°C. Phase analysis of a sample after 90min of reduction at 1200°C revealed two metallic phases with the two slag phases remaining. Both metallic phases contained carbon. One of them had a relatively high proportion of iron compared to the other, which was manganese rich. After reduction for 180 minutes at 1200°C the metallic phase high in manganese dominated.

At 1300°C the calcined ore was partly liquid. After reduction for 5 minutes at 1300°C large metallic regions were present together with unreduced ore. The non-metallic phase was composed of two components: slag and MnO phase. Small patches of metallic phases were present in the interior of the slag phase, indicating random nucleation of iron, similar to that encountered at1000°C and 1200°C. The results after 30 minutes of reduction showed the same phases as at 5 minutes of exposure but with a greater degree of reduction (fig. 9).

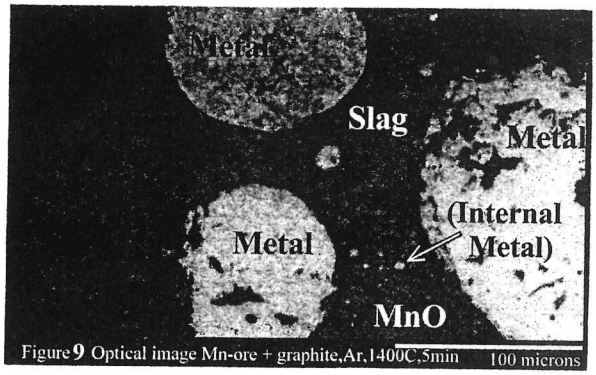

Fig. 9. Optical image Manganese ore + graphite under argon at 1400°C for 5min.

After reduction of the ore for 60 minutes at 1300°C, a small proportion of silicon (0.15%) had been reduced into the metal. After 240minutes of reduction at 1300°C microprobe analysis showed that practically all of the iron and manganese were reduced as well as some of the silicon.

At 1400°C a high degree of melting was achieved, the phases generally appeared more spherical and rounded. After only 7 minutes of reduction at 1400°C, a metallic phase, which was a carbide with a high proportion of manganese, and an oxide phase were identified. The oxide consisted of two regions, MnO and slag phase (fig. 9). After 20 minutes of reduction at 1400°C the MnO phase disappeared. At 20 minutes a considerable amount of silicon was reduced into the metal and the two metallic phases became more distinct. The main difference between them was that one contained silicon while the other did not. With further progress in reduction the metallic phase grew in size and the oxide phase decreased, mainly resulting in the further reduction of silicon into the metallic phase.

A series of BSE images were taken for samples subjected to reduction at 1350°C from 3 to 22 minutes. Two of these images are presented in figures 10 and 11. It was confirmed that the oxide phase segregated into two distinct phases, a pure MnO phase and a slag, which contained MnO as well as the other oxides such as Al_2O_3, and SiO_2. These two oxide phases were practically identical to those described at other temperatures. Samples at regular time intervals were studied by microprobe analysis and under a FESEM. Analysis data of the slag phases over time are presented in figures 12 and 13.

Manganese also reduced into the metallic phases, primarily in the vicinity of graphite particles and in the ore interior; though reduction in the vicinity of carbon was dominant. The metallic phases produced, from direct contact with graphite, were consistently manganese -iron carbides. The manganese content in the process of reduction over the time period of 3 to 22 minutes at

1350°C increases from about 60 to 67 atomic%, while the iron content decreases from about 12 to 5 atomic% accompanied by the decrease in carbon content from about 33 to 27 atomic%.

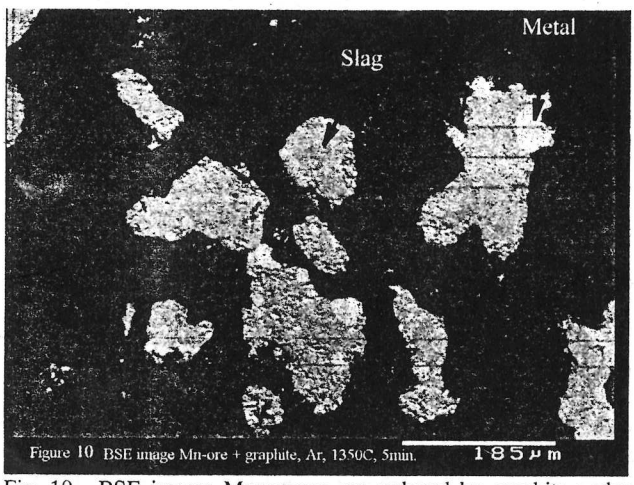

Fig. 10. BSE image: Manganese ore reduced by graphite under argon at 1350°C for 5min.

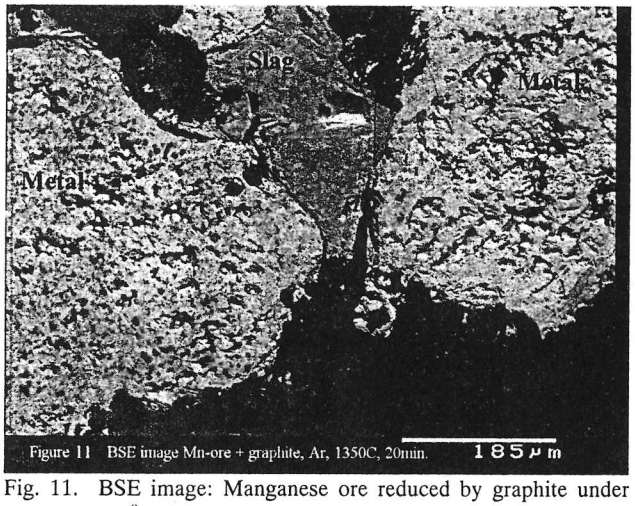

Fig. 11. BSE image: Manganese ore reduced by graphite under argon at 1350°C for 20min.

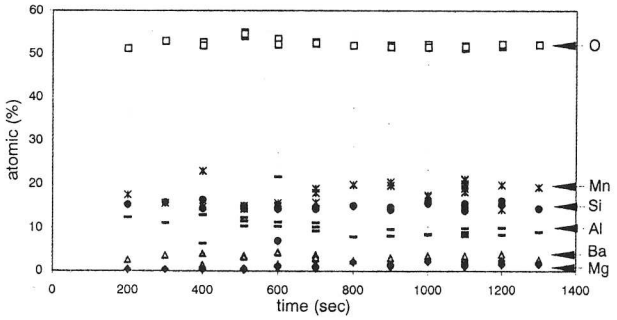

Fig. 12. Slag phase composition in the reduction of Manganese ore by graphite at 1350°C under argon.

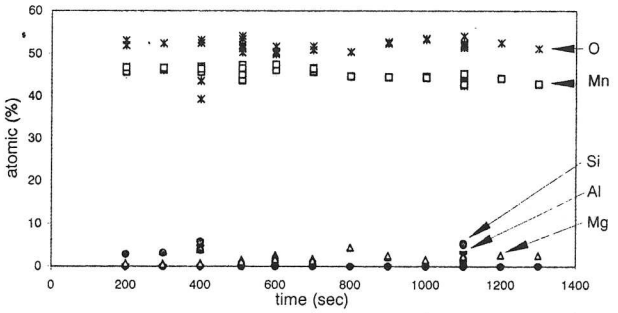

Fig. 13. Solid MnO phase composition in the reduction of Manganese ore by graphite at 1350°C under argon.

Consequently the composition of these carbides varies from the composition of $(MnFe)_7C_3$ to close to $(MnFe)_5C_2$. In the case where the metal phase was in the interior of the oxide phase and contained not only iron but also manganese the carbon content roughly corresponded to $(MnFe)_7C_3$ (fig. 14). This metallic phase in the interior of the oxide phase, contained high concentrations of metallic iron from 60 to 70% the balance being manganese.

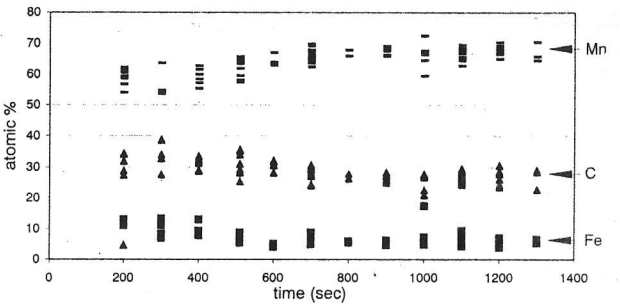

Fig. 14. Metallic phase composition in the reduction of Manganese ore by graphite at 1350°C under argon.

Reduction of FeMn slag proceeded at a much slower rate than that of Mn-ore and the phases formed during its reduction were considerably different to that of the ore. Five phases were identified at different stages of reduction, these were two slag phases, two metal phases and a SiC phase which was present at advanced stages of reduction. With increasing time and temperature the silica content of the slag decreased. Mn and Ti reported to the metal phase and S, Ca, Ba and Al remained in the slag phase. Mainly depending on the temperature, silicon was distributed between the slag, metallic and SiC phases.

Discussion

Phase analysis of manganese ore samples in the course of reduction clearly shows the coexistence of two oxide phases, which are solid MnO and a liquid (above 1200°C) oxide phase (slag) (fig. 9). The solid MnO phase during the reduction period gradually decreases in abundance and size until it has practically disappeared. During the intermediate stage of the reduction (when the solid MnO is a dominant phase) at 1350°C the manganese content of the molten slag phase remains reasonably constant between 15 and 20% (fig. 12). The MnO phase appears to slightly improve in its purity with time (fig. 13). These phases play an important role in the reduction process. The liquid slag phase may be the medium through which

the reduction occurs: originally on the graphite/oxide interface and further, as reduction progresses, on the metal/oxide interface. Transport processes are much faster in the liquid phase, than in the solid. Under such circumstances, the reduction rate may be limited by the rate of chemical reaction, which may be presented as.

$$R = k(aMnO - P_{CO}/K) \quad (1)$$

Where k is the reaction rate constant, K is the equilibrium constant for reaction (1). In experiments under argon, the second term of equation (1) may be ignored, so the rate of chemical reaction is solely dependent on the oxide phase manganese activity. The presence of the solid MnO phase sustains activity in the slag presuming that these phases are in equilibrium. The saturation of the slag with MnO depends on temperature. Thus in the presence of the solid MnO phase, MnO activity in the slag is close to 1. As the reduction proceeds, the solid MnO phase is consumed, MnO activity in the slag decreases and the rate of chemical reaction retards.

Thus, it could be expected, that if the rate of the reduction process is governed by the rate of chemical reaction, then in the presence of the MnO phase, the reduction rate will be constant, presuming that the reaction interface does not change. TGA data and analysis of CO evolution do not support this suggestion, (fig 4). The actual rate of reduction steadily decreases even in the presence of the MnO phase. This could be attributed to the change in the physical conditions of the reduction process. Both the metal and slag phases physically change as the exposure time of the dispersed powder system increases. More likely the process is under mixed controlled by the rate of chemical reaction and of "MnO" mass transfer in the liquid slag. Early in the process of reduction metallic phases appear adjacent to the MnO phases dispersed throughout the molten ore as small nucleations containing relatively large percentages of iron. These small internal metallic phases generally coalesced by the late stages of reduction. The dominant path by which the metallic phase grew was by reduction of manganese through the interface between large metal phases and molten ore. The rate of manganese vaporisation will be predominantly determined by the exposed metal surface, which appears to continuously increase through the second stage.

Effect of gas composition

Effect of CO in the gas atmosphere on the extent of ore reduction could be analysed on the basis of reaction (2) for manganese oxide reduction into metallic manganese (manganese-iron-carbon solution), or reaction (3) for reduction into manganese carbide:

$$(MnO) + C = Mn_{(metal)} + CO \quad (2)$$
$$(MnO) + 10/7C = 1/7Mn_7C_3 + CO \quad (3)$$

Increase in the CO partial pressure shifts the reactions to the left. Equilibrium constants for the reactions (2) and (2) calculated using data compiled from Knacke, Kubaschewski and Hesselmann [12] are as follows:

$$\log K_g = -14354/T + 8.48 \quad (4)$$
$$\log K_h = -13401/T + 8.32 \quad (5)$$

It follows from these equations, that reduction of MnO in the presence of the solid MnO-phase, when MnO activity is close to 1, starts at 1420°C for reaction (2) and at 1338°C for reaction (3), presuming that activities of manganese and manganese carbide in the metallic phase are 1.

When the solid MnO-phase is consumed, the extent of manganese oxide reduction from manganese ore as a function of CO partial pressure could be estimated on the basis of MnO activity in the slag (unreduced manganese) in equilibrium with the metallic phase, which may be expressed by equation (6) for reaction (2) and equation (7) for reaction (3).

$$\log a_{MnO} = 14354/T - 8.48 + \log p_{CO} \quad (6)$$
$$\log a_{MnO} = 13401/T - 8.32 + \log p_{CO} \quad (7)$$

Such assessment gives reasonable results. Manganese oxide is practically not reduced to the metallic phase under a CO atmosphere at 1300°C. The extent of reduction at 1350°C in the CO atmosphere is about 80%. Calculated a_{MnO} is 0.86 which implies that all of the MnO phase is consumed.

When the gas atmosphere is switched from CO to argon, the extent and rate of manganese reduction become significantly enhanced (fig 7). However, when argon was switched to CO gas at 1300°C, the degree of reduction changed relatively slightly, much less than in the opposite direction. This means that either the rate of oxidation of manganese carbide by CO is much slower than the rate of manganese reduction by graphite, or that this reaction is stopped by a surrounding impervious oxide layer. Further, these results indicate that the reduction of MnO to the metallic phase by graphite under the conditions of our experiments does not proceed via CO gas.

Mechanisms

In the process of Mn-ore reduction, the main reactions at 1000°C are the reduction of Fe to its metallic state and reduction of manganese oxides to MnO. It is assumed that these reactions occur via CO gas. Their rates may be limited by the Boudouard reaction.

$$C + CO_2 => 2CO \quad (8)$$

It was observed [13] that at 1000°C reduction proceeds at a faster rate with char than with graphite. Char is more reactive than graphite in respect to the Boudouard reaction. This observation supports the suggestion, that at 1000°C the rate of reduction (primarily to metallic iron and MnO) is limited by the Boudouard reaction.

The reaction at 1000°C is similar to the first stage of reduction at the higher temperatures. The rate of the first stage at the higher temperature, which is very fast, may also be rate controlled by the Boudouard reaction. The following stage is much slower.

Studies of the carbothermic reduction of pure manganese oxide at temperatures of 1070 to 1200°C by Terayama and Ikeda[12] and from 1200 to 1450°C by Rankin and van Deventer [3] have suggested that manganese reduction proceeds via CO gas, and that the rate controlling step is graphite gasification through the Boudouard reaction.

Rankin and Wynnyckyi [2], suggested that the rate of reduction is controlled by the Boudouard reaction, which is limited by CO_2 mass transfer from the reaction interface to solid carbon.

It should be pointed out that under experimental conditions employed in the current work, pure MnO is solid. Behaviour of Mn-ore and FeMn slag is quite different to pure MnO, primarily because of the formation of liquid slag phases. The Boudouard reaction would not play such an important role in the reduction of Mn-ore as in the reduction of pure MnO. This point is strongly supported by the effect of the CO content in the gas atmosphere on the rate of Mn-ore and FeMn-slag reduction. Indeed, from experimental data on Mn-ore reduction at 1350°C, presuming that MnO is reduced by the reaction:

$$MnO + 13/7CO = 1/7Mn_7C_3 + 10/7CO_2 \qquad (9)$$

the partial pressure of CO_2 generated by this reaction may be estimated from experimental data. The estimated P_{CO2} ranges from about 0.006 to 0.015atm. The equilibrium constant for the Boudouard reaction at this temperature is 4266. This means, that neither the extent, nor rate of the Boudouard reaction would be visibly affected by the change in the CO partial pressure from 0 to 1 atm. It is also unlikely that CO could significantly change the CO_2 diffusivity coefficient in the gas phase.

Using the Chapman-Enskog formula [14] the diffusivity coefficient of CO_2 in Ar at 1400°C and 1 atmosphere was estimated to be $2.49cm^2sec^{-1}$. In a CO atmosphere this coefficient is marginally higher, 2.65 cm^2sec^{-1}. So changing the gas atmosphere between Ar and CO will have little effect on the diffusion of the product gas.

Experimentally, in this study CO_2 was only detected at the very early stage of reduction, at which time manganese was not reduced into the metallic state. In this stage of reduction, as it was mentioned above manganese and iron oxides are reduced to metallic iron and MnO via CO_2 formation.

It is suggested that manganese is reduced by carbon from the liquid phase of unreduced ore, as the liquid phase has a more developed contact area with the metallic phase, and superior transport properties. This process stimulates dissolution of MnO into the slag, as the slag tends to remain saturated in MnO considering its intimate contact with the solid MnO phases (fig. 15).

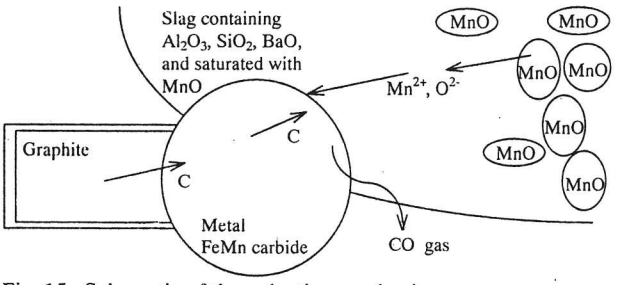

Fig. 15. Schematic of the reduction mechanism.

Features of Mn-ore and FeMn-slag reduction

Reduction of manganese ore has been compared to that of ferromanganese slag, table 1. Silica has been found to have a retarding effect on manganese reduction in the case of siliceous Mn-ore.[5] Reduction of FeMn slag is much slower than that of manganese ore. Manganese is locked up in the silicates of the slag thus inhibiting reduction. Further, upon calcination the ore has a more porous structure than the slag, thus allowing for better gas contact with the internal bulk of the particle in the early stages of reduction. Significant differences were also observed between the phases which are formed in the course of reduction (figs. 1 and 2). However, the principal mechanism of reduction through the metal / slag interface with carbon being supplied from graphite could be suggested to be common to both Mn-ore and FeMn-slag.
The following features could be outlined in terms of reduction of FeMn slag and Mn-ore.

FeMn slag reduction:
- Essentially a single phase slag from the beginning of reduction. Low manganese concentration of about 35% in the form of MnO.
- Initially contains low oxides and no iron.
- Molten slag formed after 15min of reduction at 1400°C is of the composition (atomic%): Ba 1, Ca 8, Al 9, Si 14, Mn 6, O 59.
- Spherical form of molten oxide droplets
- Graphite is not entrapped by the molten ore.
- Reduciton only occurs on the slag/graphite interface, and not internal to the oxide phase.
- Metallic phase contains a low level of carbon, less than 3%.

Mn ore reduction:
- Two oxide phases in the beginning of reduction: (i) solid MnO phase and (ii) molten slag phase of composition (atomic%): Ba 2, Al 10, Si 15, Mn 20, O 52.
- Initial ore contains higher manganese oxides in the form of Mn_2O_3 and iron.
- Irregular shape of the slag droplets.
- Graphite entrapped in the molten ore.
- Early development of metallic carbide phases well distributed within the ore interior.
- Metallic phase is a carbide of composition close to $(Mn,Fe)_7C_3$.

The effect of carbon monoxide on the rate and extent of FeMn slag reduction was observed to be dramatic with reduction at 1400°C under argon up to 3 times faster than under carbon monoxide. This very strong effect of carbon monoxide further supports the view that reduction is controlled by the chemical reaction step. Reduction essentially proceeds in a single stage unlike that encountered with the ore, which contains iron oxides, Mn_2O_3 and Mn_3O_4 oxides. The reduction of FeMn slag is considerably slower than the ore and the extent of reduction exhibits much greater variation with temperature in the case of the slag. At 1350°C the reduction of FeMn slag continues even after 2 hours with 50% reaction occurring after about 30minutes, while at the same temperature the reduction of the ore is practically completed after about 30minutes and 50% reaction is reached within about 4minutes.

Conclusion

Investigations into the reduction of manganese ores and ferromanganese slag revealed that silica has a strong retarding effect on the reduction of manganese.

Reduction of FeMn slag proceeded much slower than the ore, with both the rate and extent of reduction being strongly influenced by CO and temperature. Manganese ore after being heated above 1000°C in an inert atmosphere exhibits two separate oxide phases. This has a pronounced effect on the reduction mechanism.

Reduction of manganese ore can be divided into three stages. The first is the reduction of Fe and the higher manganese oxides to

MnO. The second being reduction of MnO from the slag phase, where it diffuses from the solid MnO-phase, the carbon being supplied by graphite contacting the metal carbide. The third, slower stage, commences upon disappearance of the MnO phase and involves the continued reduction of manganese and some silicon reduction. The final two stages are accompanied by high levels of manganese vaporisation.

On the basis of results reported in this paper for manganese ore and FeMn-slag, we could conclude that manganese oxide is reduced via the direct contact of liquid slag initially with graphite and then with the metallic phase.

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