Innovations in Ferro Alloy Industry
INFACON XI
2007

IFAPA
THE INDIAN FERRO ALLOY PRODUCERS' ASSOCIATION

KINETICS OF REDUCTION OF DIFFERENT MANGANESE ORES

Manoj Kumar, S. Ranganathan and S.N. Sinha[1]

National Metallurgical Laboratory, Jamshedpur, India
[1]Department of Metallurgical Engineering
National Institute of Technology, Jamshedpur, India
E-mail: ranganathan_sr@yahoo.co.uk

ABSTRACT

The reducibility of three different manganese ores with coke was studied. The three ores were reduced to different extents under the same experimental conditions. The investigations showed that in the temperature range of 900-1000 ×C, Fe_2O_3 in the ore was reduced to metallic iron. MnO_2 was reduced to Mn_3O_4 in all cases except one in which it was reduced to Mn_2O_3. The kinetics of reduction was controlled by different mechanisms in the different ores. Temperature had a significant influence on the reducibility of the ores.

1. INTRODUCTION

Producers of manganese alloys are forced to use ores of different grades in the submerged-arc furnace. These ores differ in their reducibility. A understanding the reducibility of the ores is crucial for controlling the operation and optimizing the process parameters. Manganese may be present as an oxide or silicate or carbonate in the ore. Development of a process to reduced the ore inside the SAF in can reduce the power consumption in the SAF. To achieve this, a thorough understanding of the reducibility of the various types of ores is required. Assessing the reducibility of different manganese ores will help the operator to understand the influence of each ore type on the process-efficiency and adopt appropriate operation procedure.

2. REDUCTION OF MANGANESE ORE

Investigations have been carried out to upgrade different types of manganese ores[1]. The ferruginous ores could be successfully upgraded by roasting at 500°C–600°C, followed by magnetic separation. TGA has been used to study the reduction of Fe_2O_3 and MnO_2 with carbon[2]. The reduction of a synthetic ore has also been investigated using the same apparatus. The haematite and goethite fractions in the ore were reduced to magnetite and MnO_2 could be reduced at 1000 °C. Charcoal was used as the reducing agent in these experiments. The Mn/Fe ratio ferruginous ores was improved in manganese ores by reduction roasting followed by magnetic separation[3]. Wood charcoal was used as the reducing agent. Eric and Burucu[4] studied the reduction of a South African ore in the temperature range 1100°C-1350°C using thermo-gravimetry. In the early stages of reduction, the higher oxide of manganese and iron, viz. Mn_2O_3 and Fe_2O_3 were reduced to MnO and FeO, respectively. This process was controlled by diffusion. Iron metallisation occurred through random nucleation. Chemical reaction between the gas phase and the oxide controlled reduction at 1350 °C. Reduction of MnO was facilitated by the dissolution of carbon in the carbide phase, $[Mn,Fe)_5C_2$. It was found that Mn_5C_2 was formed when MnO was reduced with graphite in inert atmosphere at 1200-1245°C [5]. Gasification of graphite was the rate controlling step. Addition of Fe_2O_3 to the system increased the rate of reduction remarkably. Teryama and Ideka[6] also concluded that the rate of reduction of MnO at 1070-1200°C was controlled by the rate of oxidation of carbon. The reduction product obtained was Mn_7C_3. It has been found that the extent and the rate of reduction of manganese ores were increased when the reactivity of the carbonaceous reducing agent towards CO_2 was increased[4]. It has been demonstrated that divalent manganese oxide reacted with silica in the ore to form manganese silicate. Reduction did not proceed beyond the formation of MnO in the temperature rage The three groups of manganese ores studied (siliceous, carbonate, oxide) reacted differentially upon heating. Samples which were essentially manganese oxides readily reacted to form the lower oxide at lower temperature (1150 –1200°C). The ores which were primarily carbonates reduce to the divalent oxides at higher temperatures (1150-1200°C). Manganese silicates ores were not be easily reduced by the carbothermic reduction process.

Gravimetric techniques have shown that the carbothermic reduction of manganese ores occurred in two stages[8]. In the first stages, the higher oxides were reduced to lower oxides. This process was controlled by gaseous diffusion as well as the reaction of the carbon monoxide on the pore wall of the oxide. The second stage of reduction was controlled by chemical reaction. Due to the high thermodynamic stability of MnO, manganese metal was not produced even up to 1300 °C.

At 900°C, the reduction of a siliceous ore was found to be limited to the formation of FeO from the higher oxide[9]. At 1200° and 1400°C, reduction occurred in two stages. The first stage involved the reduction of iron oxides to metallic iron and higher manganese oxide to MnO. In this stage, reduction was by CO gas. In the second stage, MnO was reduced to Mn and reduction occurred through carbon in metallic phase. A thermo-gravimetric study showed that the reduction of manganese ores was faster in argon atmosphere than in CO atmosphere[10]. However, this effect was not prominent in the early stages of reduction when iron oxide was reduced to the metal. Reduction of manganese ores with gaseous hydrogen is similar to the reduction with carbon, particularly in the early stage of the reduction and at low temperatures. The reduction of manganese ore with hydrogen at 275-400°C showed that the higher oxides were reduced through the formation of Mn_3O_4 as an intermediate phase[11].

3. EXPERIMENT

The experimental apparatus consisted of two tubular furnaces one of them containing coke maintained at 800°C. Argon gas dried by passing through a tower of $CaCl_2$ was passed through this bed of coke to remove traces of oxygen in the gas. The purified gas was passed through the main furnace containing a mixture of manganese ore and coke in a quartz capsule at the required temperature. The capsule was pushed into the constant temperature zone of the furnace as soon as the required temperature was reached. It was maintained at the temperature for the desired period of time. Then, it was quenched by rapidly pushing it for the cooler region of the furnace. The mass of the capsule at the beginning and at the end of the experimental mass were recorded.

The chemical analyses of the ores studied are given in Table 1. The coke used in these studies used contained 80.11% fixed carbon; 14.94% ash and 3.85% volatile matter. About 10 gms. of the ore was mixed with coke stoichiometrically sufficient to reduce all the iron and manganese in the ore. A schematic of the experimental apparatus is given elsewhere[12].

Some experiments were carried out to study the influence of argon flow rate on the reduction of manganese ores[13]. Petroleum coke containing 2.17% ash was used as the reducing agent. It contained about 50.5% volatile matter. Ore and coke ground to -150 mesh were thoroughly mixed and taken in a quartz capsule. 10 gm of the ore and 8 gm of coke were taken in each case.

4. RESULTS AND DISCUSSION

Experimental results are given in table 2 and 3[14]. The reduction of iron oxide can be represented by:

$$Fe_2O_3 + 3C \rightarrow 2Fe + 3CO \tag{1}$$

The reduction of manganese oxide can be represented by the following expressions:

$$2MnO_2 + C \rightarrow Mn_2O_3 + CO \tag{2}$$

$$3Mn_2O_3 + C \rightarrow 2Mn_3O_4 + CO \tag{3}$$

$$Mn_3O_4 + C \rightarrow 3MnO + CO \tag{4}$$

$$MnO + C \rightarrow Mn + CO \tag{5}$$

MnO_2 and Mn_2O_3 are not stable at temperatures above 1000 K and 1100 K, respectively, with respect to Mn_2O_3 and Mn_3O_4. Figure 1 gives the partial pressure of oxygen at equilibrium in the reactions 2-4, above. The partial pressures reach 1 atm. for the reactions 2 and 3 at 1000 K and 1100 K, respectively, MnO_2 and Mn_2O_3 decompose to the lower oxides spontaneously at these temperatures. From published literature and thermodynamic analysis, it is seen that iron oxide is reduced to the metal, at 1173 K and 1273 K, the temperatures employed in the present investigation. The reduction occurs through the formation of intermediate oxides, Fe_3O_4 and FeO. The vertical lines in the figure indicates the temperature employed in the present study. These temperatures are above the temperature of stability of the higher oxides. Hence, the state of reduction, will be controlled by the reduction of the lower oxides. Metallic manganese could not be detected in the reduced sample. The kinetics of reduction of the manganese ores was analyzed based on the following assumptions:

1. Reduction of Fe_2O_3 to the metallic state was complete.
2. Reduction of manganese oxide proceeded in steps.
3. The reduction of any lower oxide of manganese occurred after the complete reduction of the higher oxide to the lower oxidation state.

The actual mass change during reduction was computed taking the amount of volatile matter in the coke into consideration. The mass change expected due to the reduction of the MnO_2 and Mn_2O_3 to the lower oxides were evaluated in each experiment. These values were deduced from the actual mass loss due to carbothermic reduction. At 1173 K, mass balance indicated that the reduction of Fe_2O_3 to Fe was compensated as well as that of MnO_2 to Mn_2O_3. However, the latter was not completely reduced to Mn_3O_4, in the case of ore 1. The net change in mass, Δm_1, after accounting for the removal of volatile matter; the reduction of Fe_2O_3 to Fe and the reduction of MnO_2 to Mn_2O_3 is given by :

Δm_1 = observed change in the mass of the sample – change in mass due to loss of

volatile matter in coke – change in mass due to the complete reduction of

Fe_2O_3 – change in mass due to the reduction of MnO_2 to Mn_2O_3.

Δm_1, which represents the change in mass due to the reduction of Mn_2O_3 to Mn_3O_4 was found to be a function of time. The fraction reduced was given by:

$$X = \Delta m/R$$

Where R is the theoretical mass change when all the Mn_2O_3 in the sample is reduced to Mn_3O_4.

The kinetics of reduction was analyzed using the following expressions:

$$1-3(1-X)^{2/3}+2(1-X) = kt \quad (6)$$

$$1-(1-X)^{1/3} = kt \quad (7)$$

$$-\ln(1-X) = kt \quad (8)$$

$$X^2 = kt \quad (9)$$

Here, X is the fraction reduced, 't' time, in minutes and 'k', the rate constant. When the kinetics of reduction is controlled by diffusion, expression (6) is valid. When the chemical reaction controls the kinetics of reduction, the process is described by expression (7). Expression (8) and (9) describes the reduction, when reduction is controlled by reduction and by a parabolic relationship, respectively. It was found that the reduction of ore1 was best described by diffusion-controlled rate step.

In the case of ores 2 and 3, analysis of the experimental results showed that the reduction of MnO_2 to Mn_2O^3 and the latter to MnO were complete. Reduction of Mn_3O_4 to MnO was not complete. The kinetics of reduction was controlled by chemical reaction.

From the experimental data, it could be inferred that in the case of the ores, the reduction was complete up to the stage of formation of Mn_3O_4 at 1273K. However, the kinetics of reduction could not be satisfactorily described by any single mechanism. It is likely that more than one controlling step was involved.

Ore 1 has a slightly lower level of manganese and higher level of silica compared to other ores. Silica-rich ores are known to exhibit lesser reducibility compared to other types of ores. This investigation has used mass change to analyzing reducibility. More work is in progress to examine the phenomena using chemical analysis, XRD, etc.

When the rate of flow of argon gas in the reaction chamber is varied, the following reaction plays an important role in controlling the rate of reduction:

$$C + CO_2 \rightarrow 2CO \qquad (10)$$

The oxide in the ore is reduced by CO gas which is generated by the oxidation of carbon by CO_2 produced by the reduction of the oxide. The ratio of the change in the mass of the sample during the experiment to that expected for complete reduction gives the degree of reduction. Experimental data showed that under the conditions employed in this study, reduction of iron oxide to iron and that of manganese oxide to MnO were complete. The progress of reduction was analysed considering the reduction of MnO to Mn.

The fraction of reduction was defined by:

X= change in mass Äm1/(Theoretical mass change expected if all manganese oxide is reduced to metallic state.)

Where Δm1 = computed mass change for the reduction of manganese oxide

Analysis of the experimental data showed that at 1100ºC and 1150ºC, the kinetics of reduction was best represented by expression (7), when the flow rate of argon was 1 litre/minute. The reduction was controlled by chemical reaction. At other flow rates and temperatures, none of the controlling mechanisms represented by expression 6-9 could satisfactorily describe the reduction process.

Table 1: Chemical analysis of the manganese ores used in the investigations

Species	Ore 1	Ore 2	Ore 3
Mn	52.23	54.86	55.78
Fe	6.03	6.08	5.52
Si	2.36	0.65	0.36
Al	1.46	0.97	0.91
Mg	0.06	0.03	0.03
P	0.08	0.06	0.06

Table 2: Reduction at 1173 K

Ore	Time, minutes	% of Mass change
Ore 1	30	17.99
	60	18.49
	90	18.88
Ore 2	30	20.00
	60	20.52
	90	19.18
Ore 3	30	20.33
	60	20.20
	90	20.40

Table 3 : Reduction at 1273 K

Ore	Time, minutes	% of Mass Change
Ore 1	30	18.90
	60	20.90
	90	21.17
Ore 2	30	22.18
	60	22.85
	90	22.73
Ore 3	30	21.43
	60	21.54
	90	21.84

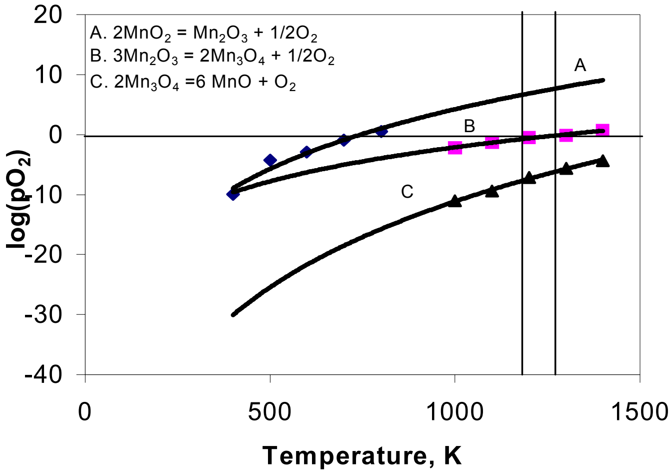

Figure 1: Equilibrium oxygen partial pressures[14]

5. CONCLUSION

The carbo-thermic reduction of three different manganese ores was studied. The degree of reduction was dependent on the nature of the ore and temperature. The process was controlled by diffusion when reduction was restricted to the stge of formation of Mn3O4. When the stage of reduction xtended up to th formation of MnO, the rte as controlled by chemical reaction. At 1173 and 1273 K, manganese metal was not formed. When the flow rate of argon over the reaction site increased, reduction proceeded up to the stahe of the formation of manganese metal. Th reduction was controlled by chemical reaction.

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