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Manganese Ore Decomposition and Carbon Reduction in Steelmaking

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Abstract: To improve the direct alloying of manganese ore in steelmaking, the decomposition and carbon reduction of manganese ore was studied using a differential thermal analyzer and resistance furnace. The remaining material after manganese ore decomposition at 1,600 °C was a mixture of 43 % MnO, 40 % MnSiO₃ and FeO, and 17 % MnSiO₃. The remaining material after the carbon reduction of the manganese ore was a mixture of metal (30.8 % Mn₇C₃ and 16.1 % FeC₃) and slag (2.5 % FeO, 5.1 % SiO₂, and 18.8 % MnO). The high-temperature (1,200 °C) decomposition and reduction of manganese ore produce manganese carbonate, manganese dioxide, and manganese salicylate sesquioxide. However, because it is not easy to decompose the manganese silicate in the manganese ore, the proportion of ore being reduced by carbon is small. Therefore, the increase of the manganese reduction of manganese silicate is critical to the direct alloying of manganese ore. Adding calcium oxide or magnesium oxide to the manganese ore improves the reduction of manganese ore, whereas adding slag from the initial stage or endpoint of the converter process has little effect on the manganese ore reduction.

Keywords: manganese ore, thermal decomposition, carbon reduction, slag

Introduction

The direct alloying of steel by manganese ore [1, 2] is not fully utilized in steelmaking [3–7] and the inefficiency of the reduction of manganese ore results in low manganese yield.

The reduction of manganese ore in the solid state [3, 6, 7, 9, 10, 12, 14] comprises three stages. In the first stage

(500–1,150 °C), MnO₂, Mn₂O₃, and Mn₃O₄ are reduced to MnO by CO gas. This stage is independent of temperature and weakly dependent on ore particle size. The second stage (1,150–1,300 °C) is that of the metal phase and begins with iron and manganese nucleation, followed by Fe–Mn carbide and silicate formation. At this stage, the reduction of MnO to manganese carbide is predominantly attributed to the reaction with CO. The chemical reaction between the oxide phase and the reducing gas in conjunction with the carbon gasification is the rate-controlling step. The third stage (1,300–1,450 °C) is the reduction of the remaining oxide by the carbon dissolved in the carbide phase. This stage is controlled by the diffusion of carbon in the carbide–oxide interface.

The production data of ferromanganese alloys [3, 4] suggest that the reduction of manganese oxides to MnO at 1,100–1,200 °C in the presence of SiO₂-bearing gangue initially forms silicates in the slag. The reduction rate of MnO by carbon at 1,370 °C is 35 %, whereas that of manganese silicate by carbon is just 5 %. Steelmaking is characterized by high temperature and oxidation conditions as well as high FeO and SiO₂ content in the slag, which hampers the reduction of manganese oxides and silicates. SHIMOO T [17] studied the rate of MnO reduction in silicate and CaO–Al₂O₃ slags at high temperature; however, the results are not applicable to steelmaking.

To obtain the decomposition and reduction framework of manganese ore under high temperature, a differential thermal analyzer and a resistance furnace were used to investigate the manganese ore decomposition and reduction in steelmaking.

Experiment

Experimental materials and preparation

The starting materials were metallurgical manganese ore powder, manganese oxides of reagent grade, manganese carbonates and silicates, reducing agents (coke powder, anthracite coal, and graphite), and converter slag. The starting materials were crushed, milled, and screened to pass through a 0.074-mm sieve and oven dried at 200 °C for 24 h.

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Figure 1: Powder X-ray diffraction pattern of the manganese ore.

The manganese ore contained 42.8 % TMn, 11.6 % TFe, 7.47 % Si, 0.13 % P, and 0.016 % S. Figure 1 shows the powder X-ray diffraction pattern and major mineral phases of the manganese ore: 14 % $3\text{Mn}_2\text{O}_3 \cdot \text{MnSiO}_3$, 32 % $3\text{Mn}_2\text{O}_3 \cdot \text{MnSiO}_3$, 15 % MnO_2 , 23 % MnCO_3 , and 16 % Fe_3O_4 . The initial and final converter slag used in the experiments contained, respectively, 36.30 % and 44.30 % CaO, 20.33 % and 14.35 % SiO_2 , 10.73 % and 11.37 % MgO, 20.33 % and 14.60 % TFe, 2.20 % and 3.80 % P_2O_5 , and the slag basicity was 1.78 and 3.09.

Experimental equipment and method

A synchronous thermal analyzer and resistance furnace were used in the experiments. The analyzer simultaneously performs thermogravimetric (TG) and differential scanning thermal analysis. The samples (6–10 mg) were placed in alumina or platinum crucibles, which were then loaded in the thermal analyzer and heated from 25 °C to 1,600 °C at 10 K/min in Ar gas atmosphere with a flow

velocity of 50 ml/min. The reducing agent was graphite, anthracite, and coke. The carbon content in the raw materials was 20 %.

The samples were examined with a scanning electron microscope to obtain the slag phase composition.

Results

Thermal decomposition of manganese ore at 1,600 °C

Figure 2 shows the decomposition of manganese ore from room temperature to 1,600 °C. The total mass loss was 16.31 % and the DSC (Differential Scanning Calorimetry) data can be divided into five regions. Based on the relevant literature reports [6] and thermodynamic analysis, the following reactions may occur in the five regions of the DSC curve. Region 1 between 200 °C and 400 °C includes an endothermic and an exothermic peak. The endothermic peak is attributed to the evaporation of the adsorbed water, while the exothermic peak is due to the conversion of $\alpha\text{-MnO}_2$ to $\beta\text{-MnO}_2$. The decomposition of MnO_2 and MnCO_3 occurs in region (2), with measured mass loss of 9.43 % close to the theoretical value of 9.2 % and measured enthalpy change of 25.31 kJ/mol compared with the calculated value of 28.20 kJ/mol. The decomposition of Mn_2O_3 occurs in region (3), with measured mass loss of 3.2 % close to the theoretical value of 3.18 % and measured enthalpy change of 29.5 kJ/mol compared with the calculated value of 28.18 kJ/mol. The decomposition of $3\text{Mn}_2\text{O}_3 \cdot \text{MnSiO}_3$ and Mn_3O_4 occurs in region (4); the measured mass loss is 1.85 %, much less than the theoretical loss of 6.99 %, and the measured enthalpy is 52.46 kJ/mol, much higher than the theoretical enthalpy change of 23.73 kJ/mol. The decomposition of Fe_3O_4 occurs in region (5); the measured mass loss is 1 %, much less than the theoretical value of 6.89 %. The

Figure 2: Decomposition of Mn ore and reduction of Mn ore and graphite.

remaining material is a mixture of MnO (43 %), MnSiO₃ (40 %), and FeO (17 %).

Carbon reduction of manganese ore

Assuming that MnO₂, MnCO₃, Mn₂O₃, and Fe₃O₄ completely decomposed at 1,400 °C (in contrast to MnSiO₃), the carbon loss was 50 % and the theoretical mass loss of the manganese ore mixture was 44.2 %. Figure 2 shows that the manganese mass loss is 34.39 % at 1,400 °C. The curve in Figure 2(b) can be divided into four regions: (1) the water evaporation region, (2) the reaction of MnO₂ and carbon to produce MnO and CO, (3) the melting of MnSiO₃, and (4) the decomposition of Mn₃O₄ and the reduction of manganese oxide to Mn, i. e., $C + MnO = Mn + CO$. The remaining material was a mixture of metal (30.8 % Mn₇C₃ and 16.1 % FeC₃) and slag (2.5 % FeO, 5.1 % SiO₂, and 18.8 % MnO).

Figure 3(a) shows the effects of the different reducing agents on the reduction of manganese ore at 1,200 °C. It is seen from Figure 3(b) that the mass loss (ΔTG) of anthracite, coke, and graphite mass loss is 28.85 %, 26.7 %, and 24.31 %, respectively. After deducting the volatiles in anthracite and graphite, the largest mass loss in this mixture is that of coke, followed by that of anthracite and graphite. Clearly, coke is the best reducing agent of the three.

Decomposition products of manganese ore at 1,600 °C

Manganese ore without a reducing agent was heated at 1,600 °C under argon atmosphere for 30 min. Manganese ore (80 %) and graphite (20 %) were subsequently reacted at 1,600 °C under argon atmosphere for 30 min. In both cases, the slag samples were cooled and observed using

an optical microscope and scanning electron microscopy (SEM). The results are shown in Figures 4(a) and 4(b).

In Figure 4(a), the slag samples contain two phases in equal proportions. The chemical composition of each phase is given in Table 1. The results suggest that phase A comprises MnO, FeO, Al₂O₃, and SiO₂. The alumina is attributed to the alumina crucible. Phase A is calculated to comprise 68.4 % MnSiO₃, 18.8 % MnO, and 12.8 % FeO. Phase B comprises FeO and MnO.

In Figure 4(b), the slag samples from the carbon reduction of the manganese ore contain three phases. The third phase is the gel material for preparing the samples. The chemical composition of each phase is given in Table 1. Point A represents the carbon-rich ferromanganese phase produced by the reduction of manganese ore. Point B is a ferromanganese phase that also contains Al₂O₃, SiO₂, MnO, and FeO. Point C denotes the excess graphite after the reduction of the manganese ore. Point D mainly comprises Al₂O₃, SiO₂, and MnO.

Based on the determination of XRD in samples, semi-quantitative results were obtained. The carbon reduction products of the manganese ore were Mn₇C₃ (27.8 %) and FeC₃ (9.4 %) in the metal phase and SiO₂ (14.7 %) and MnO (43 %) in the slag.

Results and discussion

Decomposition of manganese ore at 1,600 °C

The decomposition of pure MnO₂ is shown in Figure 5(a). There are mainly three similarities with the DTA (Differential Thermal Analysis) of the manganese ore. In pure MnO₂, the decomposition of MnO₂ corresponds to peak 1, the decomposition of Mn₂O₃ corresponds to peak 2, and the decomposition of Mn₃O₄ corresponds to peak 4.

Figure 3: Comparison of the TG and DTA curves of manganese ore and carbon mixtures.

(a) Slag after manganese ore decomposition at 1600°C

(b) Slag after carbon reduction of manganese ore at 1600 °C

Figure 4: Slag after manganese ore decomposition and carbon reduction at 1,600 °C. (a) Slag after manganese ore decomposition at 1,600 °C. (b) Slag after carbon reduction of manganese ore at 1,600 °C.

Table 1: Chemical composition of the points in the SEM photos.

Figure	Point	Element (%)					
		C	O	Si	Al	Mn	Fe
4(a)	A	–	9.21	12.88	3.50	49.23	8.81
	B	–	6.02	0.16	0	61.41	8.81
4(b)	A	6.57				80.64	8.81
	B	11.73	9.71	6.87	3.58	58.80	5.72
	C	100	–	–	–	–	–
	D	14.50	37.48	26.13	15.35	3.44	0.37

The decomposition of manganese ore with 15 % MnO_2 is associated with a mass loss of 1.35 % at 550–680 °C (peak 1), mass loss of 0.45 % at 950–1,020 °C (peak 2), and mass loss of 0.63 % at 1,400–1,550 °C (peak 3). The mass losses at peaks 1, 2, and 4 are lower than the corresponding losses in the decomposition of manganese ore. Thus, MnO_2 contributes to the decomposition of the manganese ore.

The high-temperature decomposition of pure MnCO_3 is shown in Figure 5(b). Compared with the DTA of the manganese ore decomposition, the main similarity is in peak 1 that is associated with the reaction $\text{MnCO}_3 = \text{MnO} + \text{CO}_2$. Manganese ore with 23 % MnCO_3 undergoes 8.25 % mass loss at 400–600 °C (peak 1), which equals the sum of the mass loss of pure MnO_2 and the decomposed manganese ore.

The high-temperature decomposition of MnSiO_3 is shown in Figure 5(c). The main similarity with the DTA of the manganese ore is in peak 1, where MnSiO_3 melting

occurs and heat is absorbed. There is little mass loss because there are only few impurities.

The comparison of the DTA of the pure substances can help decipher the decomposition of manganese ore. In the manganese ore, MnO_2 , MnCO_3 , Mn_2O_3 , and Mn_3O_4 decompose below 1,200 °C and produce MnO that accounts for 49 % of the manganese. Fe_3O_4 decomposes to FeO at 1,400 °C, whereas the MnSiO_3 (35 %) in the manganese ore is difficult to break down. Improving this step in the reduction of the manganese ore will maximize the yield of manganese.

Effect of converter slag on carbon reduction of manganese ore

BOF (Basic Oxygen Furnace) slag from the early and interim blowing stage [18] was added to the manganese

Figure 5: DTA of pure MnO₂, MnCO₃, and MnSiO₃. (a) Decomposition of pure MnO₂, (b) decomposition of pure MnCO₃, (c) decomposition of pure MnSiO₃.

Figure 6: DTA of Mn ore, graphite, and converter slag mixture.

ore. Figure 6 shows the DTA of mixtures with 80 % manganese ore, 20 % graphite, and 10 % initial or endpoint BOF slag. The addition of initial or endpoint BOF slag has little effect on the manganese ore reduction.

Manganese ore (80 %), graphite (20 %), and converter slag (10 %) were heated at 1,600 °C under argon atmosphere for 30 min. The slag sample was then cooled and observed using an optical microscope and SEM. The results are shown as Figure 7.

In Figure 7, the slag samples of the carbon reduction of manganese ore are divided into two phases. The second phase is the gel material for preparing the samples. The chemical composition of each phase is given in Table 2.

Point A represents carbon ferromanganese and ferrosilicon phases. The composition of point B is mainly that of a ferromanganese phase with Al₂O₃, SiO₂, MnO, FeO, and CaO. Point C is mainly characterized by the presence of Al₂O₃, SiO₂, MnO, and CaO. Finally, point D represents the excess graphite after the carbon reduction of the manganese ore.

Improving the reduction of manganese in manganese ore

In the experiments, the achieved reduction rate of manganese ore was only 66 %. MnSiO₃ must be

Figure 7: Slag of manganese ore after carbon reduction with converter slag at 1,600 °C.

Table 2: Chemical composition of the points in the SEM photos.

Point	Element (%)						
	C	O	Si	Al	Mn	Fe	Ca
A	4.58		5.11		62.49	26.04	
B	10.01	25.59	23.02	19.86	4.27	0.84	16.18
C	7.17	25.90	25.20	19.27	3.85	0.85	17.70
D	100						

decomposed to increase the reduction rate of manganese ore. Figure 8 shows the DTA of the MnSiO_3 decomposition and carbon reduction in 1:1 carbon and manganese ore mixtures. The MnSiO_3 decomposition is associated with 4.19% mass loss, and some additional minor mass loss is due to impurities. The mass loss of the mixture of MnSiO_3 and graphite is 17.81% at 1,400 °C. Based on calculations, if the carbon loss is 50 %, approximately 25 % of MnSiO_3 is reduced by graphite. Therefore, the carbon reduction of MnSiO_3 is critical to the direct alloying of the manganese ore.

The results in [19] suggest that adding calcium oxide or magnesium oxide to the manganese ore contributes to the reduction of manganese ore. The added calcium or magnesium substitute for manganese in the manganese silicate to produce manganese metal.

Figure 8: The TG and DSC curves of MnSiO_3 , graphite and Mn ore, and graphite and CaO or MgO. (a) Manganese silicate and graphite, (b) graphite and Mn ore, and graphite and CaO or MgO.

According to thermodynamic calculations, the Gibbs-free energy of reactions (1) and (2) at 0–1,400 °C is less than 1. Therefore, the CaSiO_3 and MgSiO_3 phases in reactions (1) and (2) are relatively stable and can contribute to the reduction of manganese.

Figure 8(b) shows the thermal analysis of mixtures of 72.7 % manganese ore, 18.2 % graphite, and 9.1 % calcium oxide or magnesium oxide. The mass loss in the samples with CaO or MgO is higher and suggests that adding calcium oxide or magnesium oxide to manganese ore promotes the carbon reduction of manganese ore. Magnesium oxide has the most positive effect.

Conclusions

We reduced manganese ore comprising 14 % $3\text{Mn}_2\text{O}_3 \cdot \text{MnSiO}_3$, 32 % $3\text{Mn}_2\text{O}_3 \cdot \text{MnSiO}_3$, 15 % MnO_2 , 23 % MnCO_3 , and 16 % Fe_3O_4 .

MnO_2 , MnCO_3 , and Mn_2O_3 decomposed below 1,200 °C and Fe_3O_4 decomposed at 1,400 °C, whereas MnSiO_3 hardly decomposed. The remaining material was a mixture of 43 % MnO , 40 % MnSiO_3 and FeO , and 17 % MnSiO_3 .

The mass loss of manganese ore and graphite mixtures is 34.39 % at 1,400 °C, close to the theoretical value of 44.2 %. The mass loss owing to the carbon reduction of MnO_2 , MnCO_3 , and Mn_2O_3 is 70 % and 7 % because of the reduction of MnSiO_3 . The reduction products are a metal phase comprising 30.8 % Mn_7C_3 and 16.1 % FeC_3 and slag comprising 2.5 % FeO , 5.1 % SiO_2 , and 18.8 % MnO . Coke is the best reducing agent of manganese ore, followed by anthracite and graphite.

The addition of initial or endpoint BOF slag does not enhance the carbon reduction of manganese ore. In contrast, the addition of CaO or MgO does a better job, with

MgO being a better decomposition agent of manganese ore in ore and graphite mixtures.

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