Fundamental Investigation of High Temperature Reduction and Melting Behavior of Manganese Ore

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DOI: http://dx.doi.org/10.2355/isijinternational.ISIJINT-2016-568

Several studies have examined the reduction behavior of manganese ore at high temperature with the aim of reducing the manganese cost in the steelmaking process. However, the transformation behavior of manganese compounds at high temperatures had not yet been clarified. Therefore, in this paper, the effects of temperature and oxygen partial pressure, as well as chemical composition, on the transformation and melting behavior of manganese ore were investigated by using high temperature X-ray diffraction (XRD) and thermogravimetry-differential thermal analysis (TG-DTA) in order to obtain fundamental information on the pre-reduction process of manganese ore. The main manganese compound in the raw manganese ore used in this study was characterized as CaMn₆SiO₁₂ by XRD at room temperature, while the main Mn compounds in the sintered manganese ore were Mn₃O₄ and MnO. Under a vacuum condition, raw manganese ore and sintered manganese ore were reduced to MnO above 1 473 K. However, under atmospheric conditions (pressure: 760 Torr), manganese ore was reduced to Mn₃O₄ rather than MnO at temperatures above 1 073 K. The results of high temperature XRD agreed with thermodynamic calculations. The melting temperature of the raw manganese ore evaluated by TG-DTA was lower than that of the sintered manganese ore due to the difference in the manganese oxide in each ore rather than the difference in the content of gangue components such as Al₂O₃, CaO, MgO and Fe₂O₃. The higher melting temperature of the sintered manganese ore is interpreted in terms of a higher content of MnO due to heat treatment.

KEY WORDS: manganese ore; X-ray diffraction; TG-DTA; melting temperature; MnO; Mn₃O₄.

1. Introduction

In recent years, manganese and phosphorus have been added to structural steel products as solute strengthening elements to improve the strength of the steel. In the steelmaking process, manganese alloy and metallic manganese are added during BOF tapping or in the secondary refining process. Since manganese ore is a more economical manganese source than manganese alloys such as ferromanganese and metallic manganese, manganese ore is used in the steelmaking process. There are two types of manganese ore. One is raw manganese ore, and the other is sintered manganese ore. The oxygen content of raw manganese ore is higher than that of sintered manganese ore. The oxygen content of manganese ore is important in consider of the reduction behavior of the ore since the manganese yield of manganese ore decreases as the oxygen content of the ore increases. In order to increase manganese ore usage in the steelmaking process, it is important to understand the decomposition and dissolution behaviors of manganese ore at high temperature. Many studies on techniques for high temperature reduction and the gas reduction behavior of manganese ore have been reported. Terayama et al. investigated the reduction behavior of manganese oxide. When manganese ore is heated with carbon, the manganese ore is thermally decomposed and reduced to the MnO phase at around 1 200 K through interactions with CO and CO₂. Furthermore, when iron coexists with manganese and MnFe₂O₄, a FeO–MnO type nonstoichiometric compound is generated at 1 163 K; that compound is reduced to metallic iron and MnO at 1 273 K, after which reduction of MnO proceeds. Kaneko et al. investigated the change in oxygen content in manganese ore by using a 60 kg sintering simulator. In their experiments, when raw manganese ore was sintered at temperatures from 1 573 K to 1 673 K, the oxygen content in the manganese ore decreased accompanying chemical reduction from MnO₂ to Mn₃O₄ and then MnO. Kaneko et al. also reported that the melting temperature of manganese ore containing 20% CaO is 100 K lower than that of ore without CaO. However, the effect of the chemistry of the manganese oxide in manganese ore on the reduction and melting behavior of the ore has not been clarified.

In this work, the effects of temperature and oxygen...
partial pressure, as well as chemical composition, on the transformation of manganese ore were investigated in order to obtain fundamental information on the pre-reduction process of manganese ore. In addition, the effects of the kind of manganese oxide and the contents of gangue components in manganese ore on the melting behavior of the ore were also investigated.

2. Experimental Procedure

2.1. Manganese Ore

Table 1 shows the compositions of the manganese ores used in this study. A is a raw manganese ore, B is a sintered manganese ore and C is a heat-treated sintered manganese ore. The oxygen contents of ores A, B and C are 34.8%, 27.8% and 25.4%, respectively. The oxygen content of the raw manganese ore is higher than that of the sintered manganese ore, since the oxygen in the raw ore is removed in the sintering process.

Sample C was prepared by performing heat treatment of the sintered ore B in order to investigate the effect of the oxygen content in manganese ore on the melting behavior of manganese ore. Heat treatment was carried out by using a high temperature vacuum furnace under an Ar atmosphere at 1923 K. The heating rate was 5 K/min from 303 K to 1473 K and 6.5 K/min from 1273 K to 1923 K, and the cooling rate was about 3 K/min. The difference between the MgO and T.Fe contents of the sintered ore B and heat-treated ore C is due to variations in the contents of the Mn ore.

2.2. High Temperature XRD Measurement

High temperature XRD measurements were performed to investigate the change of the manganese compounds during heating. Sample A was raw manganese ore, and sample B was sintered manganese ore. Table 2 shows the experimental conditions for X-ray diffraction. Measurements were carried out under atmospheric and vacuum conditions (1 Torr) at 303 K, 1073 K, 1473 K and 1773 K. The samples were heated at a fixed heating rate of 50 K/min. Platinum was used as a substrate. X-ray diffraction was performed after holding for 5 minutes at each temperature. The obtained data were compared with those calculated by FactSage.\(^\text{12}\)

2.3. TG-DTA Measurements

TG-DTA measurements were used to investigate the effect of the chemistry of the manganese oxide in manganese ore on melting behavior. The above-mentioned sample ores A, B and C were used. The manganese ore samples were crushed and ground, and 0.1 g was placed in a platinum crucible. Both the sample and the reference material were then heated from 303 K to 1923 K at the heating rate of 10 K/min under Ar atmosphere conditions. High purity Ar gas was used to keep in Ar atmosphere.

3. Results and Discussion

3.1. Effect of Temperature and Oxygen Partial Pressure on Reduction Behavior of Manganese Ore

Figure 1 shows the results of the XRD measurement of ores A, B and C at 303 K under the atmospheric condi-

![Fig. 1. X-ray diffraction patterns of manganese ores at room temperature. A: raw manganese ore, B: sintered manganese ore, C: heat-treated manganese ore. (Online version in color.)](image)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Chemical Compound</th>
<th>T.Mn</th>
<th>T.Fe</th>
<th>SiO2</th>
<th>Al2O3</th>
<th>CaO</th>
<th>MgO</th>
<th>P</th>
<th>S</th>
<th>T.O</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Raw Mn ore</td>
<td>42.8</td>
<td>5.9</td>
<td>5.9</td>
<td>0.8</td>
<td>7.9</td>
<td>1.5</td>
<td>0.033</td>
<td>0.265</td>
<td>34.8</td>
</tr>
<tr>
<td>B</td>
<td>Sintered Mn ore</td>
<td>61.8</td>
<td>3.2</td>
<td>6.2</td>
<td>7.7</td>
<td>0.5</td>
<td>0.3</td>
<td>&lt;0.005</td>
<td>0.017</td>
<td>27.8</td>
</tr>
<tr>
<td>C</td>
<td>Heat-treated Mn ore</td>
<td>62.8</td>
<td>0.9</td>
<td>7.6</td>
<td>6.3</td>
<td>0.7</td>
<td>2.8</td>
<td>&lt;0.005</td>
<td>0.015</td>
<td>25.4</td>
</tr>
</tbody>
</table>

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The kind of manganese compounds detected in the XRD measurement were CaMn$_6$SiO$_{12}$ in the raw ore A, 2MnO·SiO$_2$ and Mn$_3$O$_4$ MnO in the sintered ore B and MnO in the heat-treated ore C. Figure 2 shows the results of the high temperature XRD measurement of ore A at elevated temperature. Under the atmospheric condition, manganese oxide did not change until 1 073 K, and only Mn$_3$O$_4$ was identified at 1 473 K. At 1 773 K, the manganese ore is considered to melt, since only the platinum used as the substrate was detected.

Under the vacuum condition, the manganese oxide in the manganese ore did not change until 1 073 K, and only MnO was detected at 1 473 K. Figure 3 shows the results of the high temperature XRD measurement of the sintered ore B. At 1 073 K, Mn$_2$O$_3$ was detected in addition to 2MnO·SiO$_2$ and Mn$_3$O$_4$, but only Mn$_3$O$_4$ was detected at 1 473 K and 1 773 K. Under the vacuum condition, the manganese oxide in the manganese ore did not change until 1 473 K, and only MnO was detected at 1 773 K. The result of the high temperature XRD measurements are summarized in Table 3. Both ore A and ore B were reduced to MnO under the vacuum condition (1 Torr) above 1 473 K. However, under the atmospheric condition (760 Torr), both manganese ores

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Chemical compound</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 473 K</td>
<td>Mn$_3$O$_4$</td>
</tr>
<tr>
<td>1 073 K</td>
<td>CaMn$<em>6$SiO$</em>{12}$, Fe$_2$O$_3$</td>
</tr>
<tr>
<td>303 K</td>
<td>CaMn$<em>6$SiO$</em>{12}$, Fe$_2$O$_3$</td>
</tr>
</tbody>
</table>

Table 3. Chemical compounds identified by X-ray diffraction at each temperature under atmospheric and vacuum conditions.

a) Sample A: raw manganese ore

b) Sample B: sintered manganese ore

Fig. 2. X-ray diffraction patterns of raw manganese ore at elevated temperature a) under atmospheric condition, b) under vacuum condition. (Online version in color.)

Fig. 3. X-ray diffraction patterns of sintered manganese ore at elevated temperature a) under atmospheric condition, b) under vacuum condition. (Online version in color.)
were reduced to Mn$_3$O$_4$ rather than MnO.

The results obtained by the high temperature XRD measurements were compared with the results calculated by FactSage. Figure 4 shows the phase stability diagram of manganese oxidation calculated by FactSage. The value of PO$_2$ was calculated by multiplying the total pressure and the oxygen concentration. In the measurement of high temperature XRD, the chamber was heated while keeping pressure constant. Manganese compounds change in the order of MnO$_2$, Mn$_3$O$_4$, Mn$_2$O$_3$, MnO and liquid phase with increasing temperature. As shown in Fig. 4, the changes in the manganese oxide detected by high temperature X-ray diffraction roughly agreed with the FactSage calculation results in the case of ore B. From these results, it is considered that the manganese ore can be defined as in an equilibrium condition during holding for 5 minutes at the specific temperature in the high temperature X-ray diffraction measurements.

3.2. Relationship between Kind of Manganese Oxide in Manganese Ore and Melting Behavior

Based on the results of the high temperature X-ray diffraction measurements, the effect of the kind of manganese oxides in the ore on the melting behavior of the ore was investigated. Figure 5 shows the results of TG-DTA measurements of the manganese ores. The weight decreased with increasing temperature. The weight decreases of ores A, B and C were about 12 mg, 5 mg and 0.5 mg respectively. It is considered that the manganese oxide of the manganese compound is decomposed and releases oxygen during heating. Because in the XRD measurement the peak of CaMn$_6$SiO$_{12}$ was disappeared and Mn$_3$O$_4$ was appeared between 1 073 and 1 473 K as shown in Fig. 2. In addition, the weight decreased from 1 500 to 1 650 K in all cases. In this temperature range, it is considered that Mn$_3$O$_4$ is decomposed into MnO. Because in the XRD measurement the peak of Mn$_3$O$_4$ was disappear and MnO was appeared above 1 500 K as shown in Fig. 3. This results matches a Terayama’s report.

In addition to the TG-DTA measurements, the melting temperature was also estimated by thermodynamic calculations by FactSage. The Factsage calculations considered Mn$_2$O$_3$, Mn$_3$O$_4$, MnO, Al$_2$O$_3$, CaO, Fe$_2$O$_3$ and MgO. The melting temperature was regarded as the temperature when the solid phase fraction became zero. Table 4 shows the chemical compositions of the manganese ore used for the thermodynamic calculation by FactSage. The melting temperature of the Mn ore measured by DTA was determined in the following way. In the DTA measurement, several peaks were detected around the melting temperature calculated by FactSage, because the manganese ore is a mixture of various substances. However, since Mn compounds are the main compounds in Mn ore, it is considered that the largest peak corresponds to the melting of Mn ore. Therefore, the temperature when the micro volt change in a fixed time was largest around the calculated temperature was determined as the melting temperature of Mn ore. Figure 6 shows the melting temperature of the manganese ores determined by the DTA measurement. The melting temperatures of ores A, B and C were 1 688 K, 1 732 K and 1 884 K, respectively. The melting temperature of the heat-treated ore C was highest of the three manganese ores. Table 5 shows a comparison of the measured and calculated melting temperatures of the three manganese ores. The difference of melting temperature between TG-DTA results and thermodynamic calculation is due to the heating rate of TG-DTA. In the case of the sintered ore B, the measured melting temperature obtained

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mn$_2$O$_3$</th>
<th>Mn$_3$O$_4$</th>
<th>MnO</th>
<th>SiO$_2$</th>
<th>Al$_2$O$_3$</th>
<th>CaO</th>
<th>MgO</th>
<th>Fe$_2$O$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A Raw Mn ore</td>
<td>71.5</td>
<td>0.0</td>
<td>0.0</td>
<td>6.9</td>
<td>0.9</td>
<td>9.2</td>
<td>1.7</td>
<td>9.8</td>
</tr>
<tr>
<td>B Sintered Mn ore</td>
<td>0.0</td>
<td>18.0</td>
<td>62.8</td>
<td>6.2</td>
<td>7.7</td>
<td>0.5</td>
<td>0.3</td>
<td>4.6</td>
</tr>
<tr>
<td>C Heat-treated Mn ore</td>
<td>0.0</td>
<td>0.0</td>
<td>81.3</td>
<td>7.6</td>
<td>6.3</td>
<td>0.7</td>
<td>2.8</td>
<td>1.3</td>
</tr>
</tbody>
</table>

Table 4. Chemical compositions of manganese ore used for thermodynamic calculation by FactSage.
by TG-DTA was 100 K higher than that of the raw ore A. The difference in the melting temperatures of A and B was thought to be due to minor elements. In order to confirm the effect of minor elements, the melting temperatures with different s of \( \text{Al}_2\text{O}_3, \text{CaO}, \text{Fe}_2\text{O}_3, \) and \( \text{MgO} \) were calculated by using FactSage under the same \( \text{PO}_2 \) as TG-DTA.

Figure 7 shows the results of the calculation. It was found that the melting temperature increased with increasing contents of \( \text{CaO} \) and \( \text{MgO} \) and decreased with increasing \( \text{Al}_2\text{O}_3 \) and \( \text{Fe}_2\text{O}_3 \).

The reason for the different melting temperatures of the raw ore A and the sintered ore B was considered. Figure 8 shows the relationship between \( \text{Mn}_2\text{O}_3/(\text{Mn}_2\text{O}_3+\text{Mn}_3\text{O}_4+\text{MnO}) \) and the calculated melting temperature when the ratio of \( \text{Mn}_3\text{O}_4 \) and \( \text{MnO} \) was constant at 0.29. The calculated melting temperature decreased when the ratio of \( \text{Mn}_3\text{O}_4 \) was increased in the range between \( \text{Mn}_3\text{O}_4=0 \) and 0.5. When the \( \text{Mn}_3\text{O}_4 \) ratio exceeded 0.5,

Table 5. Melting temperature of manganese ore determined from DTA measurement and calculated by thermodynamic calculation.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Thermodynamic calculation</th>
<th>DTA</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1768 K</td>
<td>1688 K</td>
</tr>
<tr>
<td>B</td>
<td>1845 K</td>
<td>1732 K</td>
</tr>
<tr>
<td>C</td>
<td>2012 K</td>
<td>1884 K</td>
</tr>
</tbody>
</table>

Fig. 7. Effect of CaO, MgO, Al\(_2\)O\(_3\) or Fe\(_2\)O\(_3\) concentration on melting temperature of manganese ore. (Online version in color.)

Fig. 8. Effect of \( \text{Mn}_2\text{O}_3/(\text{Mn}_2\text{O}_3+\text{Mn}_3\text{O}_4+\text{MnO}) \) ratio on melting temperature of manganese ore. (Online version in color.)
the calculated melting temperature did not change greatly. The melting temperatures of MnO, MnO$_2$, and Mn$_2$O$_3$ have been reported to be 2 123 K, 1 973 K$^1$, and 1 853 K$^{14}$ respectively. Therefore, the ratio of Mn$_3$O$_4$, which has the lowest melting temperature among the three oxides, would have an influence of lowering the melting temperature of the ore. The difference between the two calculated lines in Fig. 8 was regarded to be due to the effect of chemical components other than the components of manganese oxide. In summary, it was found that the melting temperature of the raw manganese ore was lower than that of the sintered manganese ore. The difference between the two calculated lines in Fig. 8 was considered.

**Figure 9** shows the relationship between Mn$_3$O$_4$/MnO and the calculated melting temperature.

As shown in the Table 5, the MgO content of the heat-treated ore C was higher than that of the sintered ore B, and the Fe$_2$O$_3$ content of C was lower than that of B. According to Fig. 7, the increase of MgO and decrease of Fe$_2$O$_3$ would cause the increase in the melting temperature.

Therefore, it is considered that the calculated melting temperature of the heat-treated ore C is higher than that of the sintered ore B. In addition, the melting temperature decreases as the Mn$_3$O$_4$/MnO ratio decreases. The difference in the calculated melting temperatures of B and C, which is caused by the difference in the Mn$_3$O$_4$/MnO ratio, is also shown in Fig. 9.

In summary, it was found that the melting temperature of the heat-treated ore C was the highest of the three manganese ores due to the difference in the relative contents of the manganese oxides (i.e., ratio of MnO, Mn$_2$O$_3$ and Mn$_3$O$_4$) rather than the effect of differences in the contents of gangue components such as Al$_2$O$_3$, CaO, MgO and Fe$_2$O$_3$.

### 4. Conclusion

The effects of temperature and oxygen partial pressure, as well as chemical composition, on the transformation and melting behavior of manganese ore were investigated by using high temperature X-ray diffraction (XRD) and thermogravimetry-differential thermal analysis (TG-DTA) in order to obtain fundamental information on the pre-reduction process of manganese ore. The conclusions are summarized as follows.

(1) The main manganese compound in the raw manganese ore used in this study was characterized as Ca$_4$Mn$_5$SiO$_9$ by XRD at room temperature, while the main Mn compounds in the sintered manganese ore were Mn$_3$O$_4$ and MnO. Under a vacuum condition, raw manganese ore and sintered manganese ore were reduced to MnO above 1 473 K. However, under atmospheric conditions (pressure: 760 Torr), manganese ore was reduced to Mn$_3$O$_4$ rather than MnO at temperatures above 1 073 K. The results of high temperature XRD and the results of thermodynamic calculations were in good agreement.

(2) The melting temperatures of the raw ore A, sintered ore B and heat-treated ore C evaluated by TG-DTA were 1 688 K, 1 732 K and 1 884 K, respectively. It was found that the melting temperature of ore C was the highest of the three manganese ores due to the difference in the relative contents of the manganese oxides (i.e., ratio of MnO, Mn$_2$O$_3$ and Mn$_3$O$_4$) rather than the effect of differences in the contents of gangue components such as Al$_2$O$_3$, CaO, MgO and Fe$_2$O$_3$.

### REFERENCES