Fundamental Investigation of Reduction and Dissolution Behavior of Manganese Ore at High Temperature

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1. Abstract

The high temperature reduction behavior of manganese ore was investigated with the aim of utilizing ore as a more economical manganese source in the steelmaking process. The melting temperature and phase change behaviors of raw and sintered manganese ores were measured by high temperature X-ray diffraction and DTA in the temperature range from 303K to 1773K under atmospheric and vacuum conditions. The melting temperatures of the raw and sintered manganese ores were 1688K and 1732K, respectively. The main manganese compounds in the raw and sintered manganese ores were $CaMn_6SiO_{12}$ and MnO, Mn_3O_4 respectively. Under a vacuum (0.13kPa), both the raw and sintered manganese ores were reduced to MnO above 1473K, whereas under the atmospheric condition (101.3kPa), the manganese ores were reduced to Mn_3O_4 rather than MnO. The obtained results were discussed from a thermodynamic viewpoint.

2. 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 [1]. In the steelmaking process, manganese alloy and metallic manganese are added during BOF tapping or in the secondary refining process [2]. Manganese ore is a more economical manganese source than manganese alloys such as ferromanganese and metallic manganese. 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 [3-8]. 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 1200 K through interactions with CO and CO_2[9-10]. Furthermore, when iron coexists with

manganese and $MnFe_2O_4$, a FeO-MnO type nonstoichiometric compound is generated at 1163K; that compound is reduced to metallic iron and MnO at 1273K, after which reduction of MnO proceeds[11]. Kaneko et al.[8] investigated the change in oxygen content in manganese ore by using a 60kg sintering simulator. In their experiments, raw manganese ore was sintered from 1573K to 1673K, the oxygen content in the manganese ore decreased with chemical reduction from MnO_2 to Mn_3O_4 and then MnO. Kaneko et al.[8] also reported that the melting point of manganese ore containing 20% CaO is 100K lower than that of ore without CaO. However, the effect of the chemistry of manganese oxide in manganese ore on reduction and melting behavior has not been clarified.

  In this work, the melting temperature and phase change behaviors of manganese ore were measured by high temperature X-ray diffraction and TG-DTA in the temperature range from 303K to 1773K under atmospheric and vacuum conditions.

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 and B is a sintered manganese ore. The oxygen content of the raw manganese ore is higher than that of the sintered manganese ore, since the oxygen in the raw manganese ore is removed in the sintering process.

2.2. High Temperature XRD Measurement

  High temperature XRD measurements were performed to investigate the change of manganese compound 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 (101.3kPa) at 303K, 1073K, 1473K and 1773K. The samples were heated at a fixed heating rate of 50K/min. X-ray diffraction was

Table 1 Chemical compositions of raw, sintered and heat-treated manganese ores and phases detected by X-ray analysis at room temperature

(mass%)

	Sample	Chemical Compound	T.Mn	T.Fe	SiO_2	Al_2O_3	CaO	MgO	P	S	T.O
A	Raw Mn ore	$CaMn_6SiO_{12}$	42.8	9.4	5.9	0.8	7.9	1.5	0.033	0.265	34.8
B	Sintered Mn ore	$2MnO \cdot SiO_2$, Mn_3O_4, MnO	61.8	3.2	6.2	7.7	0.5	0.3	<0.005	0.017	27.8

Table 2 Experimental conditions
for X-ray diffraction

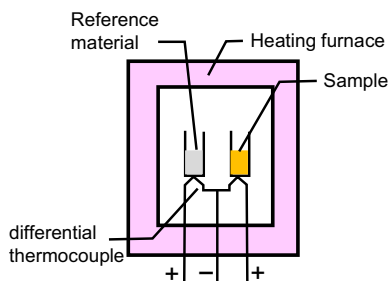| Radiation source	Cu
Voltage	45kV
Electric current	40mA
Degree(2θ)	10～60°
Presure	Atmosphere（760Torr） Vacuum（1Torr）
Temperature	303K 1073K 1473K 1773K
Holding time	5min.

Figure 1 Schematic drawing of TG-DTA
measurement method

performed after holding for 5 minutes at each temperature. The obtained data were compared with those calculated by FactSage.

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. **Figure 1** shows a schematic drawing of the TG-DTA measurement method. Raw manganese ore and sintered manganese ore were used. The manganese ore samples were crushed and ground, and 0.1g was then placed in a platinum crucible. Both the sample and the reference material were then heated from 303K to 1923K at the heating rate of 10K/min in the Ar atmosphere.

3. Results and Discussion

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

 Figure 2 shows the results of the high temperature XRD measurement of A (raw manganese ore). At 303K, only $CaMn_6SiO_{12}$ was detected. Under the atmospheric condition, manganese oxide did not change until 1073K, and only Mn_3O_4 was identified at 1473K. At 1773K, the manganese ore is considered to melt, since only the platinum used as a substrate was detected. Under the vacuum condition, the manganese oxide in the manganese ore did not change until 1073K, and only MnO was detected at 1473K. **Figure 3** shows the results of the high temperature
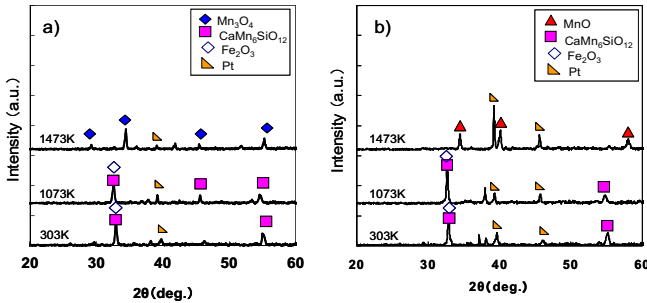
Figure 2   X-ray diffraction patterns of raw manganese ore at elevated temperature
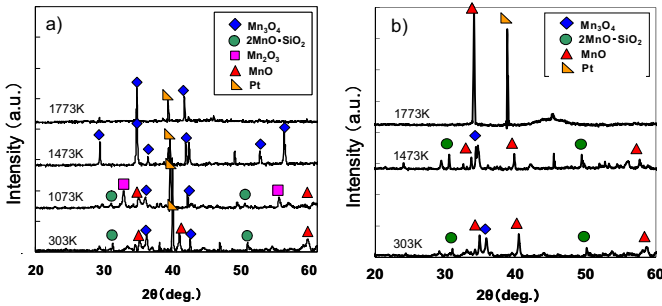a) atmospheric condition, b) vacuum condition

Figure 3   X-ray diffraction patterns of sintered manganese ore at elevated temperature
a) atmospheric condition, b) vacuum condition

XRD measurement of B (sintered manganese ore). $2MnO \cdot SiO_2$, Mn_3O_4 and MnO were identified at 303K. At 1073K, Mn_2O_3 was detected in addition to $2MnO \cdot SiO_2$ and Mn_3O_4. Only Mn_3O_4 was identified at 1473K and 1773K. Under the vacuum condition, the manganese oxide in the manganese ore did not change until 1473K, and only MnO was identified at 1773K. The results obtained by high temperature XRD measurement were compared with the results calculated by FactSage. **Figure 4** shows the phase diagram of manganese oxidation calculated by Factsage. Manganese compounds change in the order of MnO_2, Mn_2O_3, Mn_3O_4, 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 (sintered manganese ore).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. The results revealed

that both the raw ore and the sintered ore were reduced to MnO under the vacuum condition (0.13kPa) above 1473K. However, under the atmospheric condition (101.3kPa), both manganese ores were reduced to Mn_3O_4 rather than MnO.

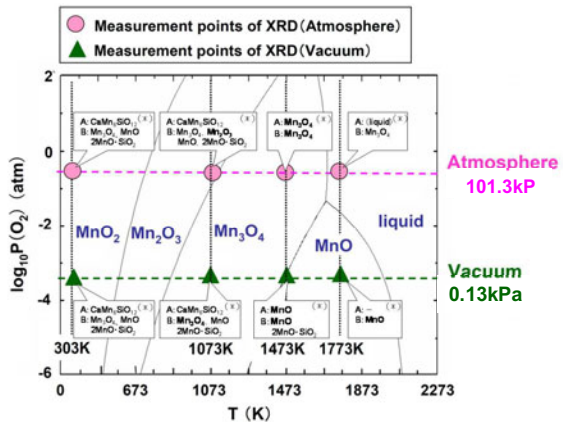3.2. Relationship Between Kind of Manganese Oxide in Manganese Ore and Reduction Behavior

Figure 4 Phase stability diagram of Mn-O system

Based on the results of the high temperature X-ray diffraction measurements, the effect of the kind of manganese oxides in the ore on melting behavior was investigated. **Figure 5** shows the results of TG-DTA measurements of the manganese ores. Weight decreased with increasing temperature. The weight decrease of the raw ore A was about 12mg while that of the sintered ore B was about 5mg. The amount of oxygen in the raw ore A is larger than that in the raw ore B. Therefore, the difference of the weight decrease between raw ore A and B is caused by the amount of release of oxygen during thermal decomposition of manganese compounds According to Fig.4, thermal decomposition of
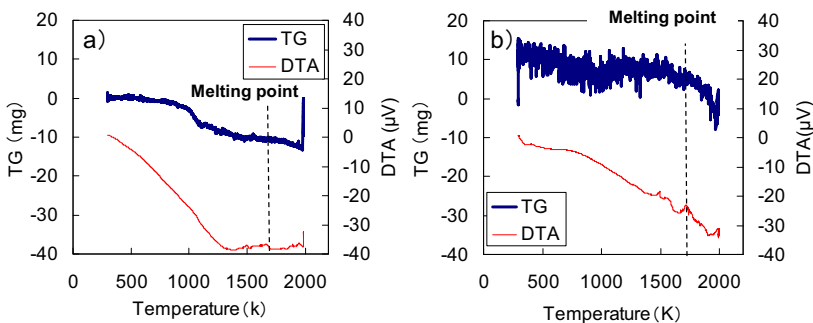

Figure 5 TG-DTA curves of manganese ore in Ar gas atmosphere, a) raw manganese ore,
　　　b) sintered manganese ore

$CaMn_6SiO_{12}$ and Mn_3O_4 generation take place at 1000K in the case of the raw ore A. In both cases of the raw ore A, and the sintered ore B, Mn_3O_4 decompose to MnO in the range between 1500 and 1650K. So, it is considered that the raw ore A, and the sintered ore B are reduced during heating in TG-DTA measurements. In the TG-DTA measurements, the largest peak during measurement was regarded as its melting points, although the amounts of solidus and liquidus ratio at the peak was unknown. The melting points obtained by TG-DTA of raw ore A and

Figure 6 Melting point of manganese ore determined by DTA measurement

B were 1688 and 1732, respectively. Those melting points were compared with those calculated by FactSage. The Factsage calculation considered Mn_2O_3, Mn_3O_4 and MnO and SiO_2, Al_2O_3, CaO, Fe_2O_3, and MgO. In the FactSage calculations, melting points were regarded as a liquidus. **Figure 6** shows a comparison of the measured and calculated melting points of the manganese ores. The TG-DTA measurement results and thermodynamic calculation results were in good agreement. The Factsage calculation considered Mn_2O_3, Mn_3O_4 and MnO and SiO_2, Al_2O_3, CaO, Fe_2O_3, and MgO. In the FactSage calculations, melting points were regarded as a liquidus. In the case of ore B, the measured melting temperature obtained by TG-DTA was 100K higher than that of ore A. The difference in the melting points of A and B was thought to be due to minor elements. To confirm the effect of minor elements, the melting points were calculated for different ratios of Al_2O_3, CaO, Fe_2O_3, MgO, and SiO_2 by using FactSage. **Figure 7** shows the results of these calculations. It was found that the melting point increased with increasing contents of CaO and MgO and decreased with increasing Al_2O_3, Fe_2O_3 and SiO_2. The reason for the different melting points of A (row manganese ore) and B (sintered manganese ore) was considered. **Figure 8** shows relationship between Mn_2O_3 /($Mn_2O_3+Mn_3O_4+MnO$) and the calculated melting points when the ratio of Mn_3O_4 and MnO was constant at 0.29. The calculated melting point decreased when the ratio of Mn_2O_3 was increased in the range between Mn_2O_3=0 and 0.5. When the Mn_2O_3 ratio exceeded 0.5, the calculated melting point did not change greatly. The melting points of MnO, Mn_3O_4 and Mn_2O_3 were reported to be 2123K[13], 1973K[7] and 1853K[13], respectively. Therefore, the ratio of Mn_2O_3 , which has the lowest melting point among the three oxides, would have an influence on lowering the melting point. The difference between the two calculated lines in **Fig. 8** was regarded as the effect of chemical components other than the components of manganese oxide. In summary, it was found that the melting point of the raw manganese ore was lower than that of the sintered
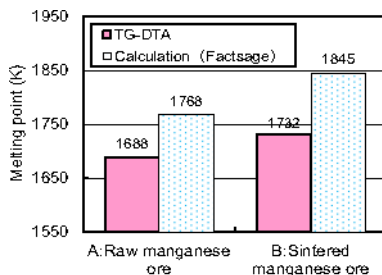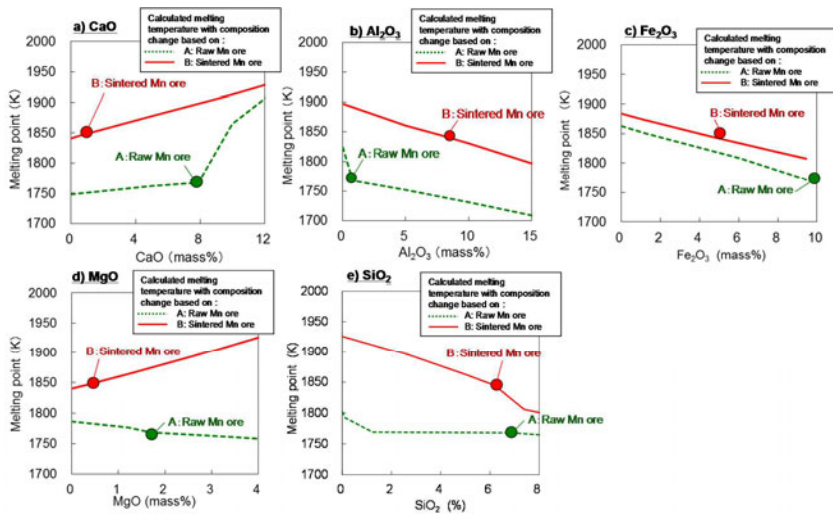
Figure 7 Effect of CaO, MgO, Al_2O_3, SiO_2 and Fe_2O_3 concentration on melting point of mnganese ore

manganese ore due to the difference in the relative contents of the manganese oxides (i.e., ratio of Mn_2O_3) rather than the effect of differences in the contents of gangue components such as Al_2O_3, CaO, MgO, SiO_2 and Fe_2O_3.
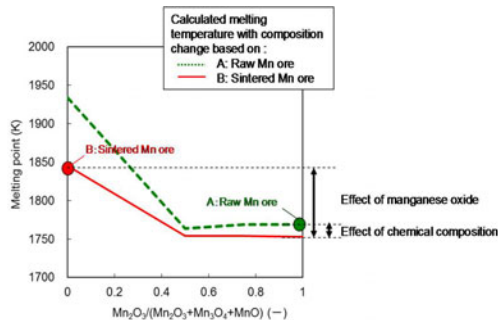

Figure 8 Effect of ratio of Mn_2O_3 to $(Mn_2O_3+Mn_3O_4+MnO)$ on melting point of

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 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 $CaMn_6SiO_{12}$ by XRD at room temperature, while the main Mn compounds in the sintered manganese ore were Mn_3O_4 and MnO. Under a vacuum condition, raw manganese ore and sintered manganese ore were reduced to MnO above 1473K. However, under atmospheric conditions (pressure: 101.3kPa), manganese ore was reduced to Mn_3O_4 rather than MnO at temperatures above 1073K. The results of high temperature XRD and the results of thermodynamic calculations were in good agreement.

2) The melting point of the raw manganese ore evaluated by TG-DTA was lower than that of the sintered manganese ore due to the difference in the relative contents of the manganese oxides in each ore rather than the effect of differences in the contents of gangue components such as Al_2O_3, CaO, MgO, SiO_2 and Fe_2O_3. It is considered that the higher melting temperature of the sintered manganese ore in comparison with the raw manganese ore is due to a higher content of Mn_2O_3.

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