Manganese Distribution Equilibrium between CaO–Fe₅O₃–SiO₂–MnO–P₂O₅–(Al₂O₃) Slags and Carbon Saturated Iron

Cheng-yi ZHU,1) Guang-qiang LI,1) Zhao-ping CHEN,2) Guo-jun MA1) and Jun LIU1)

1) Key Laboratory for Ferrous Metallurgy and Resources Utilization of Ministry of Education, China (Wuhan University of Science and Technology), Wuhan 430081, China. E-mail: ligq-2002@163.com; zhchyhsy-2002@163.com
2) Baoshan Iron & Steel Co., Ltd., Shanghai 201900, China.

(Received on September 10, 2007; accepted on December 3, 2007)

In order to find out the optimum thermodynamic conditions for hot metal demanganization and predict the manganese content after demanganization pretreatment, the equilibrium experiments for the measurement of manganese distribution between CaO–Fe₅O₃–SiO₂–MnO–P₂O₅–(Al₂O₃) slags with silver were carried out in an iron crucible at 1 573–1 673 K under pure argon atmosphere. The manganese contents in silver were converted to that in the carbon-saturated iron using the known thermodynamic data. The distribution ratios between slags and carbon-saturated iron were calculated. The results indicate that manganese distribution ratios increase with a decrease in slag basicity, and they increase with an increase in Fe₅O₃ content in the slags at first, then they decrease with an increase in content of Fe₅O₃. The maximum manganese distribution ratio is 576.6 with the Fe₅O₃ content of 50.30 mass% and the slag basicity of 0.27 at 1 623 K, and the correspondent manganese content in the carbon saturated iron is 0.015 mass%. The manganese distribution ratios decrease with an increase in MnO content in the slags. On the other hand, Al₂O₃ content in the slag has little influence on the manganese distribution ratios. The equilibrium manganese distribution ratios obtained in the present work were summarized as a function of slag compositions and temperature by the multiple regression method.

KEY WORDS: CaO–Fe₅O₃–SiO₂–MnO–P₂O₅ slags; hot metal pre-treatment; thermodynamics; silicon steel; manganese distribution ratio.
and phosphorus distribution between FeO rich slags and carbon-saturated liquid iron, respectively. Although their slag composition range was narrow and a molybdenum crucible was used in Sobandi’s experiments, their experimental methods and results are helpful to the investigation of manganese and phosphorus equilibrium between high FeO content slags and carbon-saturated liquid iron.

To find out the suitable flux and the thermodynamic conditions for demanganization and predict the manganese content after hot metal demanganization pretreatment, the manganese distribution experimentally determined manganese contents in slags and carbon-saturated iron, respectively. The experimental temperature was controlled and measured by two S type thermocouples, respectively. The experimental temperature was controlled within ±2 K by a PID controller. Pure iron crucibles were used as experimental crucibles (28 mm in outer diameter, 7 mm in inner diameter, and 70 mm in height).

3. Experimental

3.1. Equipments

A vertical type of electric resistant furnace heated by MoSi2 heating elements with an alumina reaction tube (90 mm in outer diameter, 80 mm in inner diameter, and 845 mm in height) was employed. The experimental crucibles were used as experimental crucibles (28 mm in outer diameter, 24 mm in inner diameter, and 70 mm in height).

3.2. Experimental Materials

Argon gas (99.999%) was flowed through the reaction tube during the experiments. Reagent grades of Fe2O3, MnO, CaO, SiO2, Ca3(PO4)2, and Al2O3 powders were uniformly mixed to form the slags for the experiments. Iron oxide, FeO, was prepared by reaction between Fe2O3 and Fe powders in a pure iron crucible in an argon atmosphere at 1573 K. The powders of CaO and Ca3(PO4)2 were dried at 1273 K to remove H2O and CO2. Manganese oxide, MnO, was prepared by decomposing MnCO3 at 1573 K, 1623, and 1673 K, respectively. The temperature was controlled and measured by two S type thermocouples, respectively. The experimental temperature was controlled within ±2 K by a PID controller. Pure iron crucibles were used as experimental crucibles (28 mm in outer diameter, 24 mm in inner diameter, and 70 mm in height).

Table 1. The impurity contents of the iron crucible (×10\(^{-4}\) mass%).

| Element | C | Si | P | Mn | S | N |
|---------|---|----|---|----|---|---|
| content | 80 | 20 | 60 | 170 | 50 | 80 |
was in the range from 2.41 to 19.31 mass%.

3.3. Experimental Procedures

Two steps for every experiment were taken to ensure the equilibrium between CaO–FeO–SiO₂–MnO–P₂O₅–(Al₂O₃) slags with liquid silver. At first, fifteen grams of slag was placed in an iron crucible and melted at 1 673 K for 1 h and then reacted for 10 h at experimental temperature to ensure the equilibrium between the Fe₂O containing slag and the iron crucible. After this step, the slag along with the crucible was taken out, and then immersed into water for quenching with the protection of argon gas flow. Then the slag was taken out from the iron crucible and crushed. Secondly, eight grams of the crushed previous slag equilibrated with iron crucible and fifteen grams silver were placed in another iron crucible and put back to the same furnace. In this step, the slag and silver was reacted at experimental temperature for 12 h. The time needed to reach the equilibrium in each steps was determined by preliminary experiments. After the second step experiment, the slag along with the crucible was quenched, the slag was ground. Then, the chemical compositions of the slag and manganese in silver were analyzed. Manganese in silver and slags were analyzed by ICP-AES. Total Fe content was determined by chloride titanium and potassium dichromate titration method, Fe⁺⁺, metal Fe were determined by potassium dichromate titration method, and Fe⁺⁺⁺ was obtained by subtracting Fe⁺⁺ and metal Fe contents from total Fe content.

4. Results and Discussion

4.1. Effect of the Slag Basicity on the Distribution Ratios of Manganese between CaO–FeO–SiO₂–MnO–P₂O₅ Slags and Carbon-saturated Iron

The experimental condition and the composition of slags and metal are listed in Table 2.

The effect of basicity of the slags on the equilibrium distribution ratios of manganese between CaO–FeO–SiO₂–MnO–P₂O₅ slags and carbon-saturated iron was calculated from the experimental data. The distribution ratios of manganese are plotted against the slag basicity $R$, which is defined as mass percent of CaO divided by mass percent of SiO₂, as shown in Fig. 1(a). Although the FeO content varied not so largely from 68.23 to 79.17 mass%, manganese distribution ratios decreased from 520.1 to 104.0 when the slag basicity increased from 0.19 to 3.30 at 1 573 K. This table presents the experimental condition and the composition of slags and metal.

### Table 2

| No. | Temp. (K) | $R$ | FeO (mass%) | SiO₂ (mass%) | CaO (mass%) | P₂O₅ (mass%) | Al₂O₃ (mass%) | MnO (mass%) | $[\text{Mn}^{\text{Mn}}]$ (mass%) |
|-----|-----------|-----|-------------|--------------|-------------|--------------|--------------|-------------|-----------------|
| 1   | 1.19      | 68.23 | 8.25        | 18.09        | 2.09        | -            | 2.62         | 0.0080        | 152.5           |
| 2   | 1.15      | 68.57 | 12.19       | 13.97        | 1.74        | -            | 2.86         | 0.0061        | 218.4           |
| 3   | 0.51      | 69.07 | 17.63       | 9.05         | 1.76        | -            | 2.41         | 0.0037        | 303.0           |
| 4   | 0.19      | 69.53 | 21.51       | 4.08         | 1.60        | -            | 2.79         | 0.0025        | 520.1           |
| 5   | 1.71      | 71.13 | 8.99        | 15.4         | 1.44        | -            | 2.69         | 0.0043        | 290.8           |
| 6   | 0.75      | 73.54 | 12.58       | 9.46         | 1.39        | -            | 2.73         | 0.0040        | 317.6           |
| 7   | 0.37      | 74.40 | 15.70       | 5.85         | 1.38        | -            | 2.48         | 0.0029        | 398.5           |
| 8   | 3.30      | 78.34 | 4.01        | 13.23        | 1.22        | -            | 2.91         | 0.0130        | 104.0           |
| 9   | 1.25      | 78.83 | 7.56        | 9.46         | 1.29        | -            | 2.63         | 0.0062        | 197.0           |
| 10  | 0.53      | 79.17 | 10.72       | 5.70         | 1.27        | -            | 2.87         | 0.0051        | 261.5           |
indicates that an acidic slag with high FeO content has a strong demanganization ability which is the same trend as shown in the other studies. Because MnO is a basic oxide and combined with the acidic components in the slags, higher basicity has no advantage for demanganization. The higher the basicity is, the lower the equilibrium distribution ratio of manganese is. Similar results have also been obtained when FeO contents vary from 31.87 to 72.63 mass%, as shown in Figs. 1(b), 1(c) and 1(d) investigated at 1 623 and 1 673 K, respectively.

4.2. Effect of FeO Content on the Equilibrium Distribution Ratios of Manganese between CaO–FeO–SiO2–MnO–P2O5 Slags and Carbon-saturated Iron

The effect of FeO content in slag on the equilibrium distribution ratios of manganese between slags with different basicities and carbon-saturated iron is illustrated in Figs. 2(a) and 2(b). It indicates that the manganese distribution ratio increases with FeO content to a peak at first and then decreases at an approximate constant basicity. Although the activity coefficient of manganese oxide was increased with the increase of FeO content, FeO provides more oxygen and increases the oxygen potential which benefits for manganese oxidization. Therefore increasing FeO content in some degree is beneficial to demanganization. Iron scale is a main component of demanganization flux for hot metal in the practical operation. However, excessive FeO addition may increase the melting point of flux, which deteriorates demanganization kinetic condition.

4.3. Effect of Al2O3 Content on Manganese Distribution Ratios between CaO–FeO–SiO2–MnO–P2O5–(Al2O3) Slags and Carbon-saturated Iron

The effect of Al2O3 content in slag on the equilibrium distribution ratios of manganese between slags and carbon-saturated iron is shown in Fig. 3. It indicates that Al2O3 content in the slags has little influence on the manganese distribution ratio when the other conditions are unchanged since Al2O3 in the slag behaves as a neutral oxide.

4.4. Effect of MnO Content on Manganese Distribution Ratios between CaO–FeO–SiO2–MnO–P2O5 Slags and Carbon-saturated Iron

The effect of MnO content in slag on the equilibrium dist-
4.5. Effect of Temperature on Manganese Distribution Ratios between CaO–Fe₂O₃–SiO₂–MnO–P₂O₅ Slags and Carbon-saturated Iron

The oxidation of manganese in hot metal is an exothermic reaction so that the equilibrium distribution ratios of manganese are expected to decrease with an increase in temperature, as can be seen from Fig. 5. In Fig. 5, at a nearly constant MnO content (about 3.0 mass%) and in a narrow Fe₂O₃ content range (67.44 to 72.63 mass%), the equilibrium distribution ratio of manganese between slags and carbon saturated iron has an approximately linear rela-
tionship with the temperature, which is the same trend as that reported by Jung et al.9) The effect of slag basicity on the equilibrium distribution ratios of manganese also can be seen from this figure. Therefore, hot metal treatment at a suitable temperature level is very important for demanganization in the practical process to ensure a high efficiency of demanganization.

4.6. Relationship of Equilibrium Distribution Ratios of Manganese with Composition of Slags, Temperature and Basicity

Based on the experimental results, logarithms of equilibrium quotient \( K'_{\text{Mn}} \) obtained in the present work are regressed as a linear function of slag compositions and the reciprocal of temperature by the multiple regression method. The equation is as follows and the correlation coefficient is 0.95.

\[
\log K'_{\text{Mn}} = \frac{2850.2}{T} + 0.1132(\%\text{FeO}) + 0.1334(\%\text{SiO}_2) + 0.1177(\%\text{CaO}) + 0.1717(\%\text{P}_2\text{O}_5) + 0.1204(\%\text{MnO}) - 0.1113(\%\text{CaO}) \frac{(\%\text{SiO}_2)}{(\%\text{SiO}_2)} - 12.697
\]

The logarithms of \( K'_{\text{Mn}} \) obtained by experiments are plotted against those calculated by the multiple regression Eq. (9), as shown in Fig. 6. It can be seen that the regressed equation can express the experimental results well.

In order to compare the present research results with the other researchers, \( \log L_{\text{Mn}} \) was calculated using Eq. (9) and plotted against the mass percent of (T.Fe) in the slags at 1623 K when (\%P_2O_5) is 2, (\%MnO) is 3, 10, 20 and the basicity \( R = 0.5, 1.0, 2.0 \), respectively, which is shown in Fig. 7. According to by Suito et al.7) report, the oxygen potential is controlled Fe/FeO in hot metal demanganization pretreatment. Sobandi et al.12) and Suito et al.7) also calculated \( L_{\text{Mn}} \) according to their experiments results with carbon content, [\%C], of 4.77 and 3.5, respectively, which are also plotted in Fig. 7. It indicates that the results reported by Suito et al.7) is similar to the present results when (\%T.Fe) in the slag is below 15. The present \( \log L_{\text{Mn}} \) obtained changes less than that of Suito's results with an increase in (\%T.Fe). The difference probably lies in the higher interface oxygen potential in Suito's work where FeO containing slag was brought to equilibrium with liquid iron which had lower carbon content. When \( R = 1.0 \), Sobandi's results are in good accordance with the present work. However, their calculated curves are higher than the present work at \( R = 0.8 \) and lower than this work at \( R = 1.5 \). Ogawa et al.18) did hot metal pretreatment dephosphorization experiments in an 8 t BOF with 6 t hot metal. The manganese distribution ratios between their experimental slag and liquid iron are plotted against (\%T.Fe) in the slag, which are expressed by the shadow area in Fig. 7. Their results have good accordance with the present work. It can also be seen from Fig. 7 that the influence of FeO content
in the slag on the distribution ratios at low basicity is more significant than that of at high basicity. Low basicity has strong demanganization ability at the same FeO content. The (%T.Fe) of the slag at the range from 10 to 30% has strongest demanganization ability if the basicity is constant. It seems that higher basicity slags need more FeO content to get high demanganization ability. It can be seen that the $L_{Mn}$ value is strongly dependent on the total Fe content rather than the MnO content. Furthermore, the good agreement between the present results and the plant data implies that the manganese distribution in practical operation seems to be controlled by the oxygen potential determined by the Fe/FeO equilibrium in the slag/metal interface at a given slag composition, as reported by Suito et al.\textsuperscript{7)} At the same time, the manganese distribution ratio decreases with increase of MnO content in the slags which also can be seen in Fig. 7.

5. Conclusions

The equilibrium distribution ratios of manganese between the CaO–FeO–SiO$_2$–MnO–P$_2$O$_5$–(Al$_2$O$_3$) slags and silver were measured at 1 573 K, 1 623 K, and 1 673 K. These distribution ratios were converted to that between the slags and carbon saturated iron at the same temperature by using the relevant thermodynamic data. The following conclusions can be summarized.

(1) The equilibrium quotient $K'_{Mn}$ of manganese between slags and carbon saturated iron obtained in the present work can be expressed by the following multiple regression equation:

$$
\log K'_{Mn} = \frac{2850.2}{T} + 0.1132(\%\text{FeO}) + 0.1334(\%\text{SiO}_2)
+ 0.1177(\%\text{CaO}) + 0.1717(\%\text{P}_2\text{O}_5)
+ 0.1204(\%\text{MnO}) - \frac{0.1131(\%\text{CaO})}{(\%\text{SiO}_2)} - 12.697
$$

(2) The manganese distribution ratio increases with the decrease of the slag basicity and increases with increase of FeO content in the slags at first, and then decrease with the increase of the content of FeO. The slag with the content of T.Fe ranging from 10 to 30% has the strongest demagnization ability at a constant basicity.

(3) The equilibrium distribution ratios of manganese between slag and carbon saturated iron decrease with the increasing temperature having an almost linear relationship.

(4) The manganese distribution ratios decrease with increase of MnO content in the slags slightly, while Al$_2$O$_3$ content in the slag has little influence on the manganese distribution ratios.

(5) The maximum manganese distribution ratio is 576.6 when the FeO content is about 50.30 mass% and slag basicity is 0.27 at 1 623 K, and the correspondent manganese content in the carbon saturated iron is 0.015 mass%.

REFERENCES

1) H. Suito, R. Inoue and M. Takada: Trans. Iron Steel Inst. Jpn., 21 (1981), 250.
2) T. B. Winkler and J. Chipman: Trans. AIME, 67 (1946), 111.
3) H. Suito and R. Inoue: Trans. Iron Steel Inst. Jpn., 24 (1984), 257.
4) E. T. Turkdogan: BOF Steelmaking, R. D. Pehlke, W. F. Porter, R. F. Urban and J. M. Gaines, eds., Iron Steel Soc. AIME, New York, (1975), 1.
5) E. T. Turkdogan: Physical Chemistry of High Temperature Technology, Academic Press, New York, (1980), 15.
6) A. T. Morales and R. J. Fruehan: Metall. Mater. Trans. B, 28B (1997), 1111.
7) H. Suito and R. Inoue: ISIJ Int., 35 (1995), 266.
8) S. X. Guo and Y. C. Dong: J. Iron and Steel Res., 9 (1997), 5.
9) S.-M. Jung: ISIJ Int., 43 (2003), 216.
10) R. Inoue and H. Suito: Trans. Iron Steel Inst. Jpn., 22 (1982), 711.
11) A. Sobandi, H. G. Katayama and T. Momono: ISIJ Int., 38 (1998), 9.
12) A. Sobandi, H. G. Katayama and T. Momono: ISIJ Int., 38 (1998), 953.
13) S.-M. Jung, S.-H. Kim, C.-H. Rhee and D.-J. Min: ISIJ Int., 33 (1993), 1049.
14) S.-M. Jung, C.-H. Rhee and D.-J. Min: ISIJ Int., 42 (2002), 63.
15) J. Im, K. Morita and N. Sano: ISIJ Int., 36 (1996), 517.
16) A. Sobandi, H. G. Katayama and T. Momono: ISIJ Int., 38 (1998), 781.
17) S. R. Simeonov and N. Sano: Trans. Iron Steel Inst. Jpn., 25 (1985), 1116.
18) Y. Ogawa, M. Yano, M. Matsuo and Y. Demoto: CAMP-ISIJ, 6 (1993), 1074.