Experimental Investigations of Phase Equilibria of MnS Containing Sub-systems in the MnO–SiO$_2$–Al$_2$O$_3$–MnS System

Dae-Hee WOO,$^1$ Youn-Bae KANG,$^2$ Henri GAYE$^1$ and Hae-Geon LEE$^1$  

$^1$Graduate Institute of Ferrous Technology (GIFT), Pohang University of Science and Technology (POSTECH), Pohang, 790–784, Korea. E-mail: hglee@postech.ac.kr  
$^2$Centre de Recherche en Calcul Thermochimique (CRCT), Département de génie chimique, École Polytechnique, Montréal, Québec, Canada, H3C 3A7.  

(Received on April 8, 2009; accepted on June 6, 2009)

Phase equilibria of the MnO–MnS, MnO–SiO$_2$–MnS, and MnO–Al$_2$O$_3$–MnS systems under low oxygen partial pressure have been experimentally investigated for the temperature range of 1 200 to 1 500°C using equilibration and quenching techniques. Equilibrium phases were analyzed by Scanning Electron Microscope, Electron Probe X-ray Microanalysis (EPMA), and Differential Thermal Analysis (DTA). Phase diagrams were successfully constructed for the systems investigated. A ternary compound in the MnO–SiO$_2$–MnS system was observed at 1 200°C and 1 250°C. No ternary compound or solid solution was observed in the MnO–Al$_2$O$_3$–MnS system. The results of the present study were critically compared with the results reported previously.

KEY WORDS: MnO–MnS system; MnO–SiO$_2$–MnS system; MnO–Al$_2$O$_3$–MnS system; phase equilibria; inclusions; oxide metallurgy.

1. Introduction

Precipitation of MnS on the MnO–SiO$_2$ inclusions has been reported to lead to the formation of Mn-Depleted Zone (MDZ) and enhance the formation of intragranular acicular ferrite which is beneficial for grain refinement of steels.\textsuperscript{1,2} In the case of free-cutting steels, MnO–SiO$_2$–(Al$_2$O$_3$)–MnS inclusions of low melting temperature are utilized as a lubricant layer between tool and chip in order to improve machinability.\textsuperscript{3,4} Due to Al in steel which is from refractory materials or an impurity of alloying metals, the inclusions inevitably contain certain amount of Al$_2$O$_3$. Therefore, inclusions mainly consist of MnO–SiO$_2$–Al$_2$O$_3$–MnS. In order to utilize inclusions more effectively, thermodynamics and phase relations in the subsystems of the MnO–SiO$_2$–Al$_2$O$_3$–MnS system should be clearly understood.

Previously, most experimental investigations\textsuperscript{5–8} on these systems have been focused in the composition ranges containing trace amount of MnS since sulfide capacity of oxide slags has been of great interest. Although there are several reports\textsuperscript{9–20} on the MnO–MnS system, those are not consistent with each other, hence it is difficult to obtain a reliable phase diagram of the MnO–MnS system. In the case of the MnO–SiO$_2$–MnS system, Koyama \textit{et al.}\textsuperscript{18} measured the solubility of MnS in the MnO–SiO$_2$ slag at the temperature range of 1 250 to 1 450°C. Hasegawa \textit{et al.}\textsuperscript{19} intensively investigated the phase equilibria at the similar temperature range. In spite of using the same experimental technique in both studies, their experimental results show disagreement to a substantial extent. For full utilization of the inclusions, phase diagram data at 1 200°C are also necessary because the inclusion chemistry and phases are heavily affected during reheating process near 1 200°C for hot rolling. In the present study, phase equilibria in the MnO–MnS, the MnO–SiO$_2$–MnS and the MnO–Al$_2$O$_3$–MnS system were experimentally determined at the temperature ranging from 1 200°C to 1 500°C.

2. Experimental

The general procedure is that mixtures of oxide and sulfide powders were equilibrated at high temperatures and subsequently quenched in ice-brine. Chemical compositions of each phase in the quenched samples were determined by electron probe microanalysis (EPMA). The experimental apparatus employed in the present study is schematically shown in Fig. 1.

Powders of MnO (99.9 mass\%, supplied by Kojundo, Japan), SiO$_2$ (99.9 mass\%, supplied by Kojundo, Japan), Al$_2$O$_3$ (99.9 mass\%, supplied by Aldrich, USA) and MnS (99.9 mass\%, supplied by Aldrich, USA) were used as starting materials. Each mixture was weighed to 0.4 g and placed in a boat made with molybdenum wire in a graphite tube, which was surrounded by a recrystallized alumina reaction tube sealed by the water-cooled brass end-cap. The boat assemblage was heated in a vertical MoSi$_2$ resistance furnace under an atmosphere of Ar gas purified passing CaSO$_4$ column, and Mg chips at 450°C. The assemblage was heated 0–50°C higher than a desired temperature for 1 h and then, cooled to the desired tempera-
ture and equilibrated by keeping from 18 to 50 h. The time for equilibration was confirmed through preliminary experiments by equilibrating two samples with different initial compositions in the SiO$_2$/MnS/Liquid co-saturation region at various temperatures. Although it was also reported that equilibrium was obtained within 16–24 h in the previous studies, the equilibration time was set to be longer than the previous studies to ensure complete equilibrium on the whole composition range investigated in the present study. Temperature was controlled within ±2°C using B-type thermocouple placed next to the samples. This working thermocouple was periodically checked against a calibrated standard thermocouple.

After equilibration, the lower end cap was opened and then, the assemblage was dropped directly from the hot zone into ice-brine. The samples were mounted with epoxy resin and polished. The electron microprobe analysis was carried out using JEOL JXA-8100 with wave-length dispersive spectroscopy (WDS). Operating condition was 15 kV accelerating voltage and 30 nA probe current. Pure MnO, SiO$_2$, Al$_2$O$_3$, and FeS$_2$ crystals supplied by JEOL Ltd. were used for manganese, silicon, aluminum and sulfur measurement, respectively. Data were refined using ZAF correction routine. The overall accuracy of the EPMA measurement was within 1 mass%. Since oxygen concentrations in oxysulfide mixtures were not directly measured by EPMA, measured Si and Al contents were assumed to be Si and Al contents in SiO$_2$ and Al$_2$O$_3$, respectively and also all sulfur in the oxysulfide was assumed to be associated with manganese. Therefore, the measured S content was interpreted exclusively as sulfur of MnS, and the same Mn content (in molal basis) was subtracted from the measured Mn content to give Mn content of MnO. For this reason, when S content exceeded Mn content (in molal basis), MnO composition in MnS phase sometimes had minus value, but even so its absolute value was less than 1 mass%. Because it was within the uncertainty of measurement, MnS phase which showed minus value in MnO composition was considered as 100 mass% MnS in the present study. Molybdenum dissolution in the samples was negligible. Even during very rapid quenching, dendritic crystals precipitated in the glassy part of some samples. In most cases, glassy parts near Mo foil did not show dendritic crystals due to rapid quenching. In a few cases, however, it was difficult to find complete glassy part, and EPMA analysis was carried out with a broad probe size (~50 mm), as done by other researchers.

The crystalline phases appeared in the present study were identified by measurement of their compositions using EPMA. Where necessary, X-ray diffraction (XRD) analysis was used to confirm the presence of certain crystalline phases. The XRD analysis was carried out with about 0.2 g of samples using Bruker AXS D8 Advance using Cu Kα radiation.

Eutectic temperatures in the MnO–MnS and the MnO–Al$_2$O$_3$–MnS systems were also obtained by differential thermal analysis (DTA, Netzsch STA 429). DTA was calibrated by measuring melting temperature of pure elements (In (156.6°C), Sn (231.9°C), Zn (419.6°C), Al (660.3°C), Au (1 064.2°C), and Ni (1 455°C) supplied by Netzsch Instrument Inc.). 20–30 mg of sample was placed in a platinum crucible and heated at the rate of 5°C/min. Although DTA signal was recorded during both heating and cooling cycles, the eutectic temperature was reduced only from the onset point of DTA signal obtained during the heating cycles.

3. Results and Discussions

Compositions of liquid and solid phases in equilibrated samples are given in the Table 1, and the typical microstructures observed using backscattered electron imaging mode of SEM are presented in Fig. 2 through Fig. 7. In the figures, glass and crystalline solid phases are clearly distinguished.

The shapes of SiO$_2$ crystals below and above the transition temperature of tridymite and cristobalite (1 467°C) are different as seen in Fig. 3 and Fig. 5. SiO$_2$ crystals shown in Fig. 3 and Fig. 4 were equilibrated at 1 250°C where tridymite is the stable form, while that in Fig. 5 was equilibrated at 1 500°C where β-cristobalite is stable form. Very distinctive shapes of the SiO$_2$ are clearly seen in the figures that β-cristobalite is globular type while tridymite is bar type with sharp facets around itself. According to previous investigations, cristobalite forms metastably at elevated temperature prior to tridymite. However, in the present study, temperature and equilibration time were enough to reach full equilibrium for SiO$_2$ phase transition (starting material was SiO$_2$ (β-quartz)). Crystal structures of the SiO$_2$ crystals were additionally confirmed using XRD in the present study. This also supports that equilibration for the samples were fully achieved in the present study.

3.1. MnO–MnS System

Figure 8 shows measured liquidus compositions and eutectic temperature of the MnO–MnS system in the present study along with available data in literatures. Details of experimental methods employed in the previous studies are presented in the Table 2 with the measured invariant points.

3.1.1. Eutectic Temperature

In the present study, the eutectic temperature obtained by DTA was 1 256±3°C. As can be seen in Table 2, this shows a good agreement with the results of Silverman (1 246±5°C) and Fischer et al. (1 260±5°C), but devia-
Table 1. Experimental data for the subsystems of the MnO–SiO$_2$–Al$_2$O$_3$–MnS system. Legend: L=liquid, MS=MnS, MO=MnO, SO=SiO$_2$, Te=Mn$_2$SiO$_4$, Rh=MnSiO$_3$, Ga=MnAl$_2$O$_4$, A=compound A.

| No. | T/C  | phases in equilibrium | Phase name | composition (mass%) |
|-----|------|-----------------------|------------|---------------------|
| 1   | 1500 | L=MO                  | L           | 49.2 50.8 0.0       |
|     |      | MO                    | 0.0         | 100.0 0.0           |
| 2   | 1500 | L=MS                  | L           | 84.2 15.8 0.0       |
|     |      | MS                    | 0.0         | 100.0 0.0           |
| 3   | 1400 | L=MS                  | L           | 78.6 21.4 0.0       |
|     |      | MS                    | 0.0         | 100.0 0.0           |
| 4   | 1400 | L=MO                  | L           | 56.3 43.7 0.0       |
|     |      | MO                    | 0.1         | 99.9 0.0            |
| 5   | 1500 | L=MO                  | L           | 62.0 38.0 0.0       |
|     |      | MO                    | 0.1         | 99.9 0.0            |
| 6   | 1300 | L=MO                  | L           | 61.7 38.3 0.0       |
|     |      | MO                    | 0.1         | 99.9 0.0            |
| 7   | 1300 | L=MS                  | L           | 68.1 31.9 0.0       |
|     |      | MS                    | 0.6         | 99.4 0.0            |
| 8   | 1200 | L=MO                  | L           | 64.7 35.3 0.0       |
|     |      | MO                    | 0.1         | 99.9 0.0            |
| 9   | 1260 | L=MS                  | L           | 63.6 36.4 0.0       |
|     |      | MS                    | 0.3         | 99.7 0.0            |

| No. | T/C  | phases in equilibrium | Phase name | composition (mass%) |
|-----|------|-----------------------|------------|---------------------|
| 10  | 1500 | L=MS                  | L           | 74.4 21.8 6.9       |
|     |      | MS                    | 9.7         | 99.3 0.0            |
| 11  | 1500 | L=MS                  | L           | 66.9 23.4 9.8       |
|     |      | MS                    | 9.9         | 99.1 0.0            |
| 12  | 1500 | L=MS+SO               | L           | 48.8 31.4 19.8      |
|     |      | SO                    | 0.1         | 99.9 0.0            |
|     |      | MO                    | 0.6         | 99.4 0.0            |
| 13  | 1500 | L=SO                  | L           | 11.5 47.4 41.1      |
|     |      | SO                    | 0.7         | 99.3 0.0            |
| 14  | 1500 | L=SO                  | L           | 24.6 42.3 33.0      |
|     |      | SO                    | 0.7         | 99.3 0.0            |
| 15  | 1500 | L=SO                  | L           | 0.0 50.4 49.6       |
|     |      | SO                    | 0.4         | 99.6 0.0            |
| 16  | 1500 | L=SO                  | L           | 33.0 37.7 33.3      |
|     |      | SO                    | 0.6         | 99.4 0.0            |
| 17  | 1500 | L=MO                  | L           | 32.3 58.8 9.7       |
|     |      | MO                    | 0.1         | 99.9 0.0            |
| 18  | 1500 | L=MO                  | L           | 0.0 76.6 23.4       |
|     |      | MO                    | 0.0         | 100.0 0.0           |
| 19  | 1500 | L=MO                  | L           | 10.5 75.0 14.5      |
|     |      | MO                    | 0.1         | 99.9 0.0            |
| 20  | 1500 | L=MO                  | L           | 42.9 53.3 3.8       |
|     |      | MO                    | 0.1         | 99.9 0.0            |
| 21  | 1250 | L=Te+Rh               | L           | 5.0 57.9 37.1       |
|     |      | Rh                    | 0.0         | 69.8 30.2           |
| 22  | 1250 | L=MO+A                | L           | 26.7 57.2 16.1      |
|     |      | A                     | 0.1         | 99.9 0.0            |
|     |      | MO                    | 9.2         | 67.1 23.7           |
| 23  | 1250 | Te+MO+A               | Te          | 0.0 69.9 30.1       |
|     |      | MO                    | 0.1         | 99.9 0.0            |
|     |      | A                     | 9.3         | 67.9 23.7           |
| 24  | 1250 | L=MS                  | L           | 58.5 38.0 3.5       |
|     |      | MS                    | 100.0       | 0.0 0.0             |
| 25  | 1250 | L=MS                  | L           | 37.1 46.3 16.6      |
|     |      | MS                    | 100.0       | 0.0 0.0             |
| 26  | 1250 | L=MS                  | L           | 23.4 49.0 26.6      |
|     |      | MS                    | 100.0       | 0.0 0.0             |
| 27  | 1250 | L=MS                  | L           | 28.7 48.6 22.7      |
|     |      | MS                    | 100.0       | 0.0 0.0             |
| 28  | 1250 | L=MS                  | L           | 43.4 43.5 11.2      |
|     |      | MS                    | 100.0       | 0.0 0.0             |
| 29  | 1250 | L=MS+SO               | L           | 16.7 48.0 33.3      |
|     |      | SO                    | 0.0         | 99.0 0.0            |
| 30  | 1250 | L=Rh+SO               | L           | 10.1 51.3 38.6      |
|     |      | Rh                    | 0.0         | 99.2 0.0            |
|     |      | MO                    | 0.0         | 33.8 66.2           |
| 31  | 1250 | L=Te                  | L           | 8.9 57.3 33.9       |
|     |      | Te                    | 0.0         | 69.1 30.9           |
| 32  | 1250 | L=Te                  | L           | 11.4 55.4 32.8      |
|     |      | Te                    | 0.0         | 69.8 30.2           |
| 33  | 1250 | L=Te+A                | L           | 23.3 46.2 19.9      |
|     |      | A                     | 9.5         | 66.7 23.7           |
|     |      | Te                    | 0.0         | 69.7 30.3           |

ISIJ International, Vol. 49 (2009), No. 10

© 2009 ISIJ

1492
tion from the temperatures reported by Andrew et al.\textsuperscript{11} (1,275±5°C) and Chao et al.\textsuperscript{16} (1,232±5°C). Andrew et al.\textsuperscript{11} claimed mutual solubility between solid MnO and solid MnS, and expected about 8 mass% solubility of MnS in MnO and about 15 mass% solubility of MnO in MnS at the eutectic temperature. On the other hand, Chao et al.\textsuperscript{16} reported at most about 2 mass% on the both sides at the eutectic temperature. In the present study, about 1 mass% solubility was detected only in MnS by EPMA analysis. However, in the whole analysis results, MnO contents in MnS phase were fluctuated within 1 mass% range not showing any trend or dependency of temperature. Therefore, it was concluded that mutual solubilities were almost negligible within the error range of EPMA analysis (±1 mass%).

3.1.2. Liquidus of MnO and MnS

As seen in Fig. 8, the MnS liquidus determined in the present study, although there are some discrepancies among previous studies, is in good agreement with those of Hasegawa et al.\textsuperscript{19} and Kim et al.\textsuperscript{20} For the MnO liquidus, on the other hand, the present study shows a significant difference from the results of previous investigators including
The MnO content in the liquidus composition at the MnO side is higher in the previous studies than in the present study at a given temperature. The same discrepancy is observed in the results of MnO–SiO2–MnS system, which will be shown later. As Kang et al.26) pointed out, the liquid composition saturated with MnO phase might have been overestimated in the previous studies18–20) possibly due to insufficient separation of solid from liquid phase in their analysis technique of the “primary phase saturating method”. The discrepancy between the results of Koyama et al.18) and Hasegawa et al.19) both of whom employed the same method for the MnS liquidus determination may explain the extent of uncertainty of this method. On the other hand, the method used in the present study (equilibration/quenching/EPMA) has an advantage in that compositions of each phase in a sample are measured and also, prevailing phase are identified by electron microscope in back scattered electron mode. This greatly reduces chances to overestimate liquid composition toward saturated solid phases. There are also significant discrepancies of MnO and MnS liquidus determined by Andrew et al.11) from those of other studies, and this is discussed in Sec. 3.2.

3.2. MnO–Al2O3–MnS System

Figure 9 shows the experimentally determined liquidus compositions and corresponding liquidus lines of the MnO–Al2O3–MnS system at 1 500°C. No ternary compound or solid solution was found in the present study. The solubility of Al2O3 increases with increasing the ratio of MnO to MnS. The effect of temperature is clearly seen in...
Fig. 10. Co-saturated compositions in the MnO–Al2O3–MnS system at various temperatures and sample compositions at which DTA analysis was performed.

In that, with decrease in temperature from 1500°C, the point where the liquid coexists with MnAl2O4 and MnO (see Point “M” in Fig. 10) sharply move away from the Al2O3 corner, and hence the liquid phase field shrinks rapidly. In other words, as the temperature decreases, addition of Al2O3 in the MnO–MnS binary liquid becomes more susceptible to precipitation of MnAl2O4. The eutectic temperature measured by DTA was 1243°C and sample compositions were shown in Fig. 10.

3.3. MnO–SiO2–MnS System

Figure 11 through Fig. 13 show liquidus compositions of the MnO–SiO2–MnS ternary system determined in the present study together with data of the previous studies18,19) for the temperature range of 1200 to 1500°C. It is noted that a ternary compound was observed at 1200°C and 1250°C as shown in Fig. 7. Its composition was determined to be 67.0 mass% MnO, 23.6 mass% SiO2 and 9.4 mass% MnS by EPMA analysis. The XRD peak of this compound did not match with any known compound available in the diffraction data of Joint Committee on Powder Diffraction Standards (JCPDS), but its composition is very similar to the compound 8MnO·3SiO2·MnS (68.0 mass% MnO, 21.6 mass% SiO2, 10.4 mass% MnS) reported by Hasegawa et al.19) at 1250°C. Intensive crystallographic study is necessary in order to reveal the exact chemistry and structure of this compound.

It is seen that the liquid phase field shrinks rapidly as the temperature decreases: it nearly disappear at 1200°C. For phase boundaries at 1250°C, the liquidus line of MnS determined in the present study is in good agreement with what was reported by Hasegawa et al.19) For the liquidus lines of other phases, however, the results determined by the present study were significantly different from the previous reports, in particular for the liquidus of MnO. This discrepancy is very noticeable at a higher temperature as seen in Fig. 13. It should be noted that the previous reports by Koyama et al.18) and Hasegawa et al.19) show much wider liquid phase field than that of the present study even though the temperature in their studies is lower by 50°C. This discrepancy is attributed to overestimation resulted from their experimental method of “primary phase saturating method”. This method is very sensitive to the accuracy of phase separation itself.

Because 1250°C is close to the measured eutectic temperature of the MnO–MnS binary system (1256°C), it is reasonable that MnO–MnS co-saturation point in the MnO–SiO2–MnS system at 1250°C should be close to the eutectic composition of the MnO–MnS binary system. The result in present study is reasonably close to the eutectic composition in the MnO–MnS system reported by several researchers15,16) including the present study. On the other hand, the MnO–MnS co-saturation point at 1250°C measured by Hasegawa et al.19) significantly deviates from the eutectic composition of the MnO–MnS binary system.
4. Conclusions

Phase equilibria of MnO–MnS, MnO–SiO₂–MnS, and MnO–Al₂O₃–MnS under reducing condition were determined experimentally in the temperature range of 1200 to 1500°C. Equilibrium phases and corresponding compositions for important boundaries were identified and measured using EPMA. In the MnO–MnS system, the eutectic temperature and composition of the MnO–MnS system were also determined to be 1256 ± 11°C and 64.1 mass% MnS. The melting temperature of MnS estimated by extrapolating the liquidus of MnS in the MnO–MnS binary system measured in the present study showed a good agreement with the value reported by Staffansson (1655 ± 5°C).

In the MnO–SiO₂–MnS system, a ternary compound was observed in the temperature range of 1200 to 1250°C. No ternary compound or solid solution was observed in the MnO–Al₂O₃–MnS systems.

REFERENCES

1) H.-S. Kim, H.-G. Lee and K.-S. Oh: Metall. Mater. Trans. A, 32 (2001), 1519.
2) J. H. Shim, Y. W. Cho, S. H. Chung, J. D. Shim and D. N. Lee: Acta Mater., 47 (1999), 2751.
3) S. V. Subramanian, H. O. Gekonde, X. Zhang and J. Gao: Ironmaking Steelmaking, 26 (1999), 333.
4) X. Zhang, H. Roelofs, S. Lemgen, U. Urlau and S. V. Subramanian: Steel Res., 75 (2004), 314.
5) K. P. Abraham, M. W. Davies and F. D. Richardson: J. Iron Steel Inst., 196 (1960), 309.
6) T. Kobayashi, K. Morita and N. Sano: Metall. Mater. Trans. B, 27 (1996), 652.
7) M. M. Nzotta, D. Sichen and S. Seetharaman: ISIJ Int., 38 (1998), 1170.
8) M. M. Nzotta: Scand. J. Metall., 26 (1997), 169.
9) J. P. Coughlin: J. Am. Chem. Soc., 72 (1950), 5445.
10) G. Rohl: Stahl Eisen, 33 (1913), 565.
11) J. H. Andrew, W. R. Maddocks and E. A. Fowler: J. Iron Steel Inst., 124 (1931), 295.
12) R. Vogel and W. Hotop: Arch. Eisenhüttenwes., 11 (1937), 41.
13) Z. Shibata: Sci. Rep. Tohoku Univ., 7 (1928), 279.
14) I. Staffansson: Metall. Mater Trans. B, 7 (1976), 131.
15) E. N. Silverman: Trans. Metall. Soc. AIME, 221 (1961), 512.
16) H. C. Chao, Y. E. Smith and L. H. Van Vlack: Trans. Metall. Soc. AIME, 227 (1963), 796.
17) W. A. Fischer and P. W. Bardenheuer: Arch. Eisenhüttenwes., 41 (1970), 119.
18) N. Koyama, F. Tsukihashi and N. Sano: Tetsu-to-Hagané, 79 (1993), 1334.
19) A. Hasegawa, K. Morita and N. Sano: Tetsu-to-Hagané, 81 (1995), 1109.
20) T. G. Kim, W. K. Lee, J. H. Park, D. J. Min and H. S. Song: ISIJ Int., 41 (2001), 1460.
21) A. Muan: J. Am. Ceram. Soc., 75 (1992), 1357.
22) Y.-B. Kang and H.-G. Lee: ISIJ Int., 45 (2005), 1543.
23) I. Abs-Wurmbach: Contrib. Mineral. Petrol., 71 (1980), 393.
24) O. W. Florke: Ber. Dtsch. Keram. Ges., 38 (1961), 89.
25) I. Barin: Thermochemical Data of Pure Substances, VCH, Weinheim, Germany, (1989), 900.
26) Y.-B. Kang and H.-G. Lee: ISIJ Int., 45 (2005), 1552.