EXPERIMENTAL INVESTIGATION OF PHASE EQUILIBRIA OF SUBSYSTEMS IN THE $MnO-SiO_2-Al_2O_3-MnS$ SYSTEM

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ABSTRACT

Phase equilibria and liquidus in sub-systems (MnO-MnS, $MnO-SiO_2-MnS$, $MnO-Al_2O_3-MnS$) of the $MnO-SiO_2-Al_2O_3-MnS$ system under reducing condition have been experimentally investigated for the temperature range of 1250 to 1500°C using equilibration and quenching techniques. Eutectic temperature in the MnO-MnS system was measured using Differential Thermal Analysis (DTA). Equilibrium phases were identified and chemical compositions of the phases were measured using Electron Probe X-ray Microanalysis (EPMA). The measured liquidus compositions were compared with previous investigations. Liquidus lines determined in the present study were different to a significant extent from previous investigations except the primary field of MnS. A ternary compound in $MnO-SiO_2-MnS$ system at 1250°C was observed. Overall, the liquidus boundaries of MnO-MnS, $MnO-SiO_2-MnS$, and $MnO-Al_2O_3-MnS$ systems were successfully determined.

INTRODUCTION

Resulfurized steels are most commonly used in the automotive and mould manufacturing industries. Because productivity is closely related to tool-life, it is important to protect tools during machining. Inclusions in steel have strong influence on tool-wear. Mn/Si deoxidation instead of Al deoxidation or Ca-treatment after Al deoxidation is performed to avoid solid Al_2O_3 inclusions which accelerate tool-wear. It is reported that MnS inclusions protect tools by breaking the chip with creating micro-crack and oxysulfide inclusions of low melting temperature make an adherent layer on the cutting edge which prevents chemical wear of tools [2, 7, 10]. In order to utilize inclusions more effectively, the composition of inclusions should be precisely controlled. In this regards, phase relations in the MnO-SiO_2-Al_2O_3-MnS system is of great importance when Mn/Si are used as deoxidizer.

METHODOLOGY

Mixtures of oxide and sulfide powders were equilibrated at high temperatures and quenched rapidly in ice-brine. Chemical compositions of each phase were analyzed by electron probe microanalysis(EPMA).

Powders of MnO(99.9 wt pct, supplied by Kosundo), SiO_2(99.9 wt pct, supplied by Kosundo), Al_2O_3(99.9 wt pct, supplied by Aldrich) and MnS (99.9 wt pct, supplied by Aldrich) were used as starting materials. Each mixture was weighed to 0.4 g and placed in a boat made from molybdenum foil (0.05 mm thick). Several boats were suspended by molybdenum wire in a graphite tube in a recrystallized alumina reaction tube sealed by the water-cooled brass end-cap and 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. Before starting equilibration, the assemblage was heated 50°C higher than desired temperature for 1 hour and then, cooled to the desired temperature and equilibrated for periods of time from 18 to 50 hours. 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 15kV accelerating voltage and 30 nA probe current. Pure MnO, SiO_2, Al_2O_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. Since oxide and sulfide concentrations in oxysulfide mixtures were not directly measured by EPMA, it was assumed that all sulfur existed as MnS with same mole of manganese and the balance of manganese existed as MnO. The average accuracy of the EPMA measurement was within 1 wt pct. Molybdenum oxide dissolution in sample was negligible.

The eutectic temperature in the MnO-MnS system was obtained by differential thermal analysis (Netzsch STA 429). 20~30 mg of sample was placed in platinum crucible and heated at the rate of 5°C. Although DTA signal was recorded during both heating and cooling, the eutectic temperature was reduced from the signal obtained during heating.

RESULTS AND DISCCUSIONS

Phase Diagram of the MnO-MnS System

Figure 1 shows experimentally determined liquidus composition of the MnO-MnS system. Previous data reported by several researchers [2, 3, 5] are also included. For the MnS liquidus line, although there are some discrepancies among previous studies, the results of the present study are in good agreement with Hasegawa *et al.* [3] and Kim *et al.* [5]. For MnO liquidus compositions, on the other hand, the present study shows a significant difference from the previous reports [3, 5]. For a given composition, the liquidus temperature was found higher in the present study. The same situation occurs in the results of MnO-SiO_2-MnS system. As Kang *et al.* [4] pointed out in the investigation of MnO-TiO_2-Ti_2O_3 system, liquid composition might be overestimated due to incomplete separation between solid and liquid phase in the *Primary phase saturating method* employed by previous studies [3, 5, 6].

For the temperature and composition of the eutectic point of the system, the present study showed a good agreement with the previous reports: Silverman [8] reported 1246±5°C and 63 wt pct MnS, and Chao *et al.* [1] reported 1232±5°C and 64 wt pct MnS. In the present study, the eutectic temperature obtained by DTA was 1256±3°C, and the composition was estimated at 64±1 wt pct. Chao *et al.* [1] claimed that the solubility of both MnO in MnS and MnS in MnO are about 2 wt pct at the eutectic temperature. However, no significant solubility was observed in the present study within the error range of EPMA analysis.

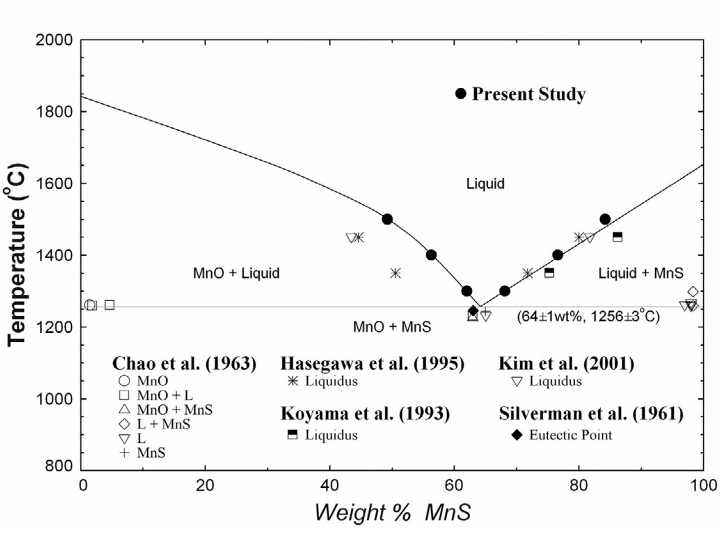
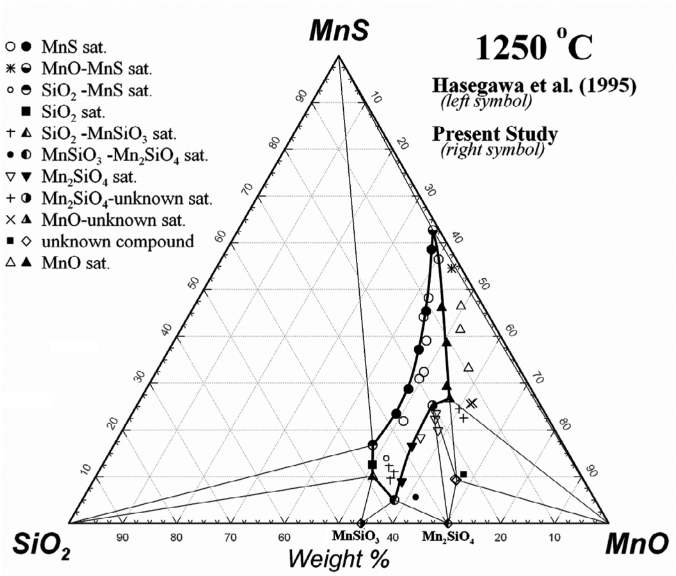


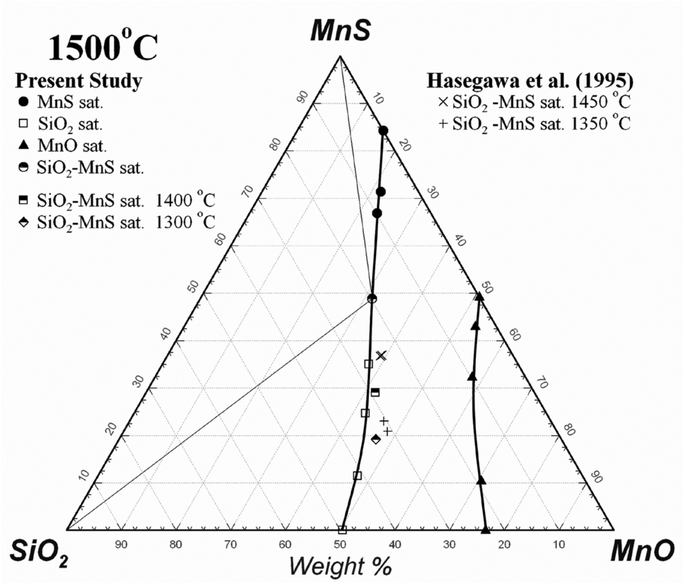
Figure 1: Phase equilibrium data in the MnO-MnS system

Phase Diagram of the MnO-SiO_2-MnS System

Figure 2 shows the experimentally determined liquidus composition in the present study from 1250 to 1500°C together with the previous data reported by Hasegawa *et al.* [3]. Microstructures of the system were observed using backscattered electron image mode of EPMA. Below 1250°C, Hasegawa *et al.* [3] reported existence of the ternary compound $8MnO \cdot 3SiO_2 \cdot MnS$ (70.0 wt pct MnO, 21.6 wt pct SiO_2, 10.4 wt pct MnS) of which XRD peak did not match with any known compound. A similar ternary compound was also found in the present study, and the EPMA analysis revealed that the ternary compound contains 67.0 wt pct MnO, 23.6 wt pct SiO_2 and 9.4 wt pct MnS which deviates to some extent from what was reported previously. For the phase boundaries, the liquidus line of MnS-saturation determined by the present study is in good agreement with what was reported by Hasegawa *et al.* [3], For the liquid lines of saturation of other phases, however, the results determined by the present study were significantly different from the previous reports.



(a) 1250°C



(b) 1500°C

Figure 2: Phase equilibrium data in the MnO-SiO_2-MnS system

In Figure 2(b), SiO_2-MnS co-saturation points at several different temperatures are included. It is seen that the co-saturation point of SiO_2-MnS moves toward the MnS corner with increasing temperature, but without noticeable change in the ratio of MnO to SiO_2(wt pct). Hasegawa *et al.* [3] also reported similar results as indicated in the figure.

Phase Diagram of the MnO-Al_2O_3-MnS System

Figure 3 shows liquidus data and estimated liquidus lines. No intermediate compound was found in this system. The solubility of Al_2O_3 increases with increasing the ratio of MnO to MnS(wt pct). There is no report on this system. When the temperature decreases from 1500 to 1400°C, the Al_2O_3 content in the liquid at the $MnAl_2O_4$-MnO co-saturation point sharply decreases, and hence the liquid phase field shrinks rapidly.

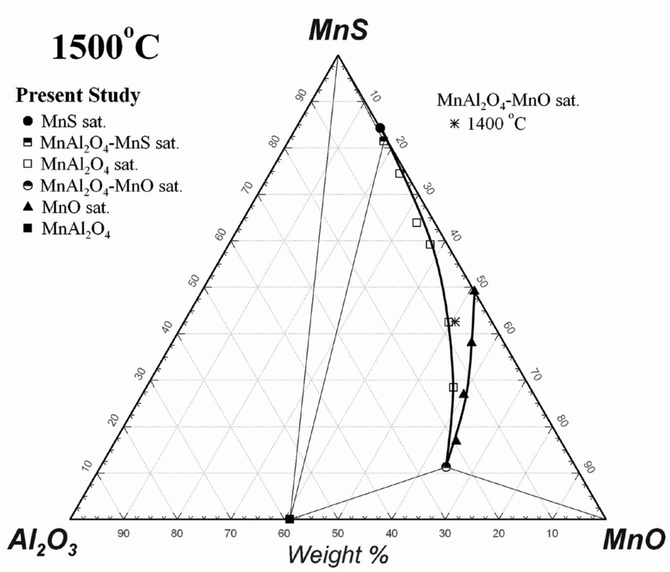


Figure 3: Phase equilibrium data in the MnO-Al_2O_3-MnS system at 1500°C

CONCLUSIONS

Phase equilibria and liquidus in sub-systems (MnO-MnS, MnO-SiO_2-MnS, MnO-Al_2O_3-MnS) of the MnO-SiO_2-Al_2O_3-MnS system under reducing condition have been determined experimentally in the temperature range from 1250°C to 1500°C. The eutectic temperature and composition of the MnO-MnS system were determined to be 1256°C and 64.5 wt pct. Equilibrium phases and corresponding compositions for important boundaries were identified and measured. A ternary compound in the MnO-SiO_2-MnS system at 1250°C was observed. Overall, the liquidus boundaries of MnO-MnS, MnO-SiO_2-MnS, and MnO-Al_2O_3-MnS systems were successfully determined. More experimental results for lower temperature of each system and a detailed discussion about formation behavior of inclusions in the steel are not shown in the present proceeding due to limited space, but will be shown in the our presentation as well as will be shown on a separate paper [9].

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