Thermodynamic Properties of the MnS–CuS$_{0.5}$ Binary System

Yun LEI, Takeshi YOSHIKAWA, Charles Q. JIA and Kazuki MORITA

1) Institute of Industrial Science, The University of Tokyo, Komaba, Meguro-ku, Tokyo, 153-8505 Japan. E-mail: leiyun@iis.u-tokyo.ac.jp, t-yoshi@iis.u-tokyo.ac.jp, kzmorita@iis.u-tokyo.ac.jp  2) Department of Chemical Engineering and Applied Chemistry, University of Toronto, 200 College Street, Toronto, Ontario, M5S 3E5 Canada. E-mail: cq.jia@utoronto.ca

(Received on December 17, 2011; accepted on February 27, 2012)

In order to discuss the formation of MnS–CuS$_{0.5}$ inclusion in γ-Fe, the phase diagram of the MnS–CuS$_{0.5}$ binary system has been determined by using a confocal scanning laser microscope (CSLM) and a chemical equilibration technique. In addition, the activities of MnS and CuS$_{0.5}$ in the liquid phase at 1 473 K were investigated by chemical equilibration with molten Cu. The phase diagram of the binary system was found to be of a eutectic type with mutual solid solubility between MnS and CuS$_{0.5}$. The activities of MnS and CuS$_{0.5}$ showed positive deviation from the ideality. Finally, the solid steel composition equilibrated with the inclusion was estimated by using the determined thermodynamic properties.

KEY WORDS: thermodynamics; phase diagram; confocal scanning laser microscope; activity; MnS–CuS$_{0.5}$; solid solubility.

1. Introduction

Steel scrap has conventionally been used as one of the main raw materials for electric arc furnace (EAF) steelmaking. However, steel scrap contains a considerable amount of copper, which is a harmful element in steel because of Cu-induced hot shortness during the heat treatment. The amount of residual copper in the steel scrap should be controlled to be less than 0.2 mass% for a practical steelmaking process.\(^1\)

Generally, it is difficult to remove copper from steel by conventional oxidation refining processes because the chemical affinity of copper for oxygen is smaller than that of iron. Copper removal from steel using sulfide fluxes, such as FeS–NaS$_{0.5}$, is a possible method for industrial applications. This method is based on the principle that the chemical affinity of copper for sulfur is stronger than that of iron for sulfur. However, copper removal by sulfide fluxes requires a large consumption of fluxes and causes an increase in the sulfur content of iron.

Recently, some researchers have reported that copper in solid steel can form copper sulfides due to its stronger affinity for sulfur, and that the copper sulfides always coexist with MnS to form complex sulfide inclusion.\(^3,4\) According to the phase diagram of the Cu–S system, CuS$_{0.5}$ is the most probable phase in the temperature range for γ-Fe.\(^5\) If copper can be stabilized as MnS–CuS$_{0.5}$ inclusion in γ-Fe, the hot shortness may be suppressed because the MnS–CuS$_{0.5}$ inclusion, unlike that of pure liquid copper, does not penetrate the grain boundaries during heat treatment. In addition, the copper sulfides coexisting with MnS inclusion were considered to work for the nucleation of acicular ferrite during the α/γ transformation, resulting in the refinement of the microstructure of steel.\(^6\) They were also expected to improve the corrosion resistance of steel.\(^7\)

In order to control the formation of MnS–CuS$_{0.5}$ inclusion in solid steel, it is necessary to know the thermodynamic properties of the MnS–CuS$_{0.5}$ binary system. Because no literature related to these properties has been reported, the phase diagram and the activities of each component in the liquid phase at 1 473 K were investigated in the present work. Moreover, the composition of the solid steel equilibrated with the MnS–CuS$_{0.5}$ inclusion was estimated by using the determined thermodynamic properties.

2. Experimental

2.1. Determination of the Phase Diagram of the MnS–CuS$_{0.5}$ Binary System

A confocal scanning laser microscope (CSLM) was employed in the present work to determine the phase diagram of the MnS–CuS$_{0.5}$ binary system. The schematic diagram of an infrared heating furnace connected with CSLM equipment is illustrated in Fig. 1. The method of operation of the CSLM to determine a phase diagram has been reported in detail in the previous work.\(^8\)

Samples were prepared by melting mixtures of reagent grade MnS and CuS$_{0.5}$ in a graphite crucible under an Ar atmosphere in an induction furnace. The Mn and Cu contents of the prepared samples were analyzed by inductively coupled plasma atomic emission spectroscopy (ICP-AES).

The prepared samples were crushed into small particles and employed for CSLM observations. In order to suppress the effects of temperature distribution due to the non-uniform heating by a halogen lamp, small-sized particles of samples (with a diameter of 1–2 mm, less than 10 mg) were subjected to observation. A prepared particle sample was charged into an Al$_2$O$_3$ crucible (O.D. 9 mm, I.D. 8 mm, height 4 mm). Prior to heating the sample, the air in the
chamber of the furnace was evacuated and the chamber was refilled with Ar gas. This process was repeated three times to ensure the complete removal of air in the chamber. The sample was subsequently heated by a halogen lamp at a heating rate of 5 K/min which was slow enough to observe "thermal arrest" (showing a constant temperature) during the phase change. The temperature was measured by using a Pt–6%Rh/Pt–30%Rh thermocouple welded to the bottom of the holder of the crucible. Temperature calibration was carried out with the melting temperatures of pure metals, namely, Ag (99.99%), Cu (99.99%), and Ni (99.9%). The accuracy of the measured temperatures was within ±3 K from the results of the measurements on the melting temperatures of the pure metals. Dissolution of Al₂O₃ from the crucible into the sulfides melt was found to be negligibly small.

The remaining samples were used to confirm the possible intermediate compound in the binary system. The samples were held in a purified Ar atmosphere at 1 200 K for 96 h and then subjected to an X-ray diffraction analysis with Cu-Kα.

A chemical equilibration technique was also employed to investigate the terminal solid solubilities of CuS₀.₅ and MnS as well as to verify the liquidus temperature measured by CSLM. A pre-melted MnS–CuS₀.₅ mixture together with a pellet of CuS₀.₅ or MnS was charged in a graphite crucible and held in a purified Ar atmosphere at 1 378 K, 1 473 K, and 1 573 K for 12 h. The pellet of MnS or CuS₀.₅ was prepared by compressing reagent grade MnS or CuS₀.₅ powder into a cylindrical shape, followed by sintering at a certain temperature (1 623 K for MnS, and 1 383 K for CuS₀.₅) in an Ar atmosphere for 3 h. The Mn and Cu contents of the liquid sulfide phase were analyzed by ICP-AES; the composition of the solid phase was determined by electron probe micro analyzer (EPMA).

### 2.2. Activity Measurement of the Liquid Sulfide Phase

The equilibration method using molten Cu as a reference metal was employed to determine the activities of the components in the liquid sulfide phase. Although copper sulfide shows the non-stoichiometric MnS–CuS₀.₅ was thus regarded to be insignificant here. A Sic electric resistance furnace connected to a proportional-integral-differential (PID) controller with a Pt–6%Rh/Pt–30%Rh thermocouple was used. Two grams of reagent grade MnS and CuS₀.₅ mixtures and two grams of Cu (99.99%) were charged into a graphite crucible and equilibrated in a purified Ar atmosphere at 1 473 K. Preliminary experiments revealed that holding for 12 h was sufficient to reach equilibrium. After equilibrium was reached, the crucible was quickly withdrawn from the furnace and quenched with water. The sulfides and the metal were carefully separated for chemical analysis. The Mn and Cu contents of the sulfides and the Mn content of the metal were analyzed by ICP-AES. The S content of the metal was analyzed by an LECO combustion analyzer. The oxidation of the sulfides and the dissolution of C from the crucible into the sulfides were insignificant as the O and C contents of the sulfides were below 0.25 mass% and 0.01 mass%, respectively.

The activities of CuS₀.₅ and MnS were determined by the following equations:

\[
\text{Cu} \left(1 + \frac{1}{2} \text{S (mass\% in molten Cu)} = \text{CuS}_0.5 \ (1)\right)
\]

\[
\Delta G_i^o = -22 470 + 14.02 T \quad (\text{J/mol})^{10,11} \quad \text{…… (2)}
\]

\[
a_{\text{CuS}_0.5} = K_i \cdot \gamma_i^{0.5} \cdot \text{[mass\%]}^{0.5} \cdot a_{\text{Cu}} \quad \text{…… (3)}
\]

\[
\text{Mn} (1) + \text{S (mass\% in molten Cu)} = \text{MnS (s)} \quad \text{…… (4)}
\]

\[
\Delta G_i^o = -204 874 + 69.15 T \quad (\text{J/mol})^{10,11} \quad \text{…… (5)}
\]

\[
a_{\text{MnS}} = K_i \cdot \gamma_i \cdot \text{[mass\%]} \cdot X_{\text{Mn}} \cdot \gamma_{\text{Mn}} \quad \text{…… (6)}
\]

where \(K_i\) and \(a_i\) are the equilibrium constant and the activity of the component \(i\), respectively; the character in the parenthesis denotes the standard state; [%] and \(X\) are the contents of \(i\) in the mass and mole percent basis, respectively; and \(f_i\) and \(\gamma_i\) are the activity coefficients of \(i\) in molten Cu at the Henrian and Raoultian standards, respectively. The activity of Cu was considered to obey Raoult’s law in molten Cu.

The activity coefficients of S and Mn were expressed...
with the first-order interaction parameters in the equations

\[
\log f_j^S = \epsilon_j S^\alpha [\% S] + \epsilon_j S^\text{Mn} [\% \text{Mn}] \quad (7)
\]

\[
\ln \gamma_{\text{Mn}} = \ln \gamma_{\text{Mn}}^\alpha + \epsilon_{\text{Mn}}^o \cdot X_{\text{Mn}} + \epsilon_{\text{Mn}}^S \cdot X_S \quad (8)
\]

where \( \epsilon_j \) and \( \epsilon_j' \) are interaction parameters of \( j \) on \( i \) in molten Cu on the mass percent and the mole fraction basis, respectively. The values of \( \epsilon_j^S, \epsilon_j^\text{Mn}, \) and \( \epsilon_j^S_{\text{Mn}} \) in molten Cu at 1473 K have been reported to be \(-0.191^\text{10}, -0.082^\text{11}\) and \(-16.1^\text{11}\) respectively. The values of \( \gamma_{\text{Mn}}^\alpha \) and \( \epsilon_{\text{Mn}}^o \) were determined in this study.

3. Results and Discussion

3.1. Phase Diagram of the MnS–CuS_{0.5} Binary System

The morphologies of a particle sample (with a diameter of 1–2 mm) during the heating process are shown in Fig. 3. Only the solid surface could be observed in the initial stage of heating, as shown in Fig. 3(a). When the temperature was increased to \( T_e \), some bright spots began to appear (Fig. 3(b)). These bright spots were tiny liquid phase. The solid phase gradually dissolved into the liquid phase and the liquid fraction increased with an increasing temperature (Fig. 3(c)). When the temperature reached \( T_m \), the solid phase disappeared and only the liquid phase could be observed, as shown in Fig. 3(d). \( T_e \) and \( T_m \) are defined as the liquid formation temperature and the liquidus temperature, respectively. The liquid formation temperature represents the eutectic temperature in the eutectic phase diagram.

In order to measure the terminal solid solubility of CuS_{0.5} and MnS by EPMA, a line analysis was conducted across the interface between the liquid and solid solution phases at the cross-sections of the samples. A typical result for the Cu-K\( \alpha \) line analysis in Fig. 4 shows a plateau region in the solid phase, in which the saturation of CuS_{0.5} was attained. An EPMA quantitative analysis was then performed for the corresponding region to measure the solid solubility of CuS_{0.5} in the MnS solid solution.

The phase diagram of the MnS–CuS_{0.5} binary system was determined by using CSLM and the chemical equilibration technique, as shown in Fig. 5. It is a eutectic phase diagram with mutual solid solubility between MnS and CuS_{0.5}. Based on the liquid formation temperatures, the eutectic temperature was determined to be 1294±22 K. Since the samples with the compositions \( X_{\text{MnS}} = 0.33 \) and \( X_{\text{MnS}} = 0.35 \) demonstrated the two lowest measured liquidus temperatures (1307 K and 1308 K, respectively), the eutectic composition was estimated to be \( X_{\text{MnS}} = 0.34±0.01 \). The solid solubilities of CuS_{0.5} in the MnS solid solutions were determined to be \( X_{\text{CuS}_{0.5}} = 0.071 \) (1378 K), \( X_{\text{CuS}_{0.5}} = 0.067 \) (1473 K), and \( X_{\text{CuS}_{0.5}} = 0.063 \) (1573 K), and that of MnS in the CuS_{0.5} solid solution was determined to be \( X_{\text{MnS}} = 0.012 \) at 1378 K.

X-ray diffraction analysis was conducted for the samples with \( X_{\text{MnS}} = 0.08, 0.36, 0.58, \) and 0.95, and only MnS and CuS_{0.5} were identified for all the samples. It was determined that there was no intermediate compound in the MnS–CuS_{0.5} binary system.

3.2. Activities of MnS and CuS_{0.5} in the Liquid Sulfide Phase at 1473 K

3.2.1. Activity Coefficient of Mn for Infinite Dilute Solution of Mn in Molten Cu at 1473 K

The activity coefficient of Mn in molten Cu was determined by equilibrating molten Cu with the sulfides melt saturated with solid MnS at 1473 K. With Eqs. (6) to (8), the activity coefficient of Mn in molten Cu (at its infinite dilution) along with the self-interaction coefficient was determined. Since the CuS_{0.5} solubility in the MnS solid solution was 0.067, as mentioned above, the activity of MnS was determined to be 0.933 by assuming that it obeys Raoult’s
law. In addition, we assumed the following relationship between \( \gamma_{\text{Mn}}^o \) and \( \varepsilon_{\text{Mn}}^\text{Ma} \), which was derived from the regular solution behavior.

\[
\varepsilon_{\text{Mn}}^\text{Ma} = -2 \ln \gamma_{\text{Mn}}^o \quad \text{.................................................. (9)}
\]

The experiment was repeated three times to ensure repeatability, and the results are listed for MnS sat.–1–3 in Table 1. The values of \( \gamma_{\text{Mn}}^o \) and \( \varepsilon_{\text{Mn}}^\text{Ma} \) were determined to be 0.197±0.006 and 3.25±0.07, respectively.

The activity coefficient of Mn in molten Cu at its infinite dilution was reported by Jung et al.\(^{12}\) for the temperature range of 1623 K to 1723 K; the activity coefficient was determined as Eq. (10) by equilibrating the copper with a solid MnO pellet in a CO–CO\(_2\) gas mixture.

\[
\log \gamma_{\text{Mn}}^o = -\frac{1437}{T} + 0.319, \quad 1623-1723 \text{ K} \quad \text{... (10)}
\]

According to Eq. (10), \( \gamma_{\text{Mn}}^o \) was calculated to be 0.221 at 1473 K, which is close to the present result. However, the activities of MnS at its saturation composition were estimated to be above unity when using this value. Therefore, the value \( \gamma_{\text{Mn}}^o = 0.197 \) is used in the following section.

### 3.2.2. Activities of MnS and CuS\(_{0.5}\) in the Liquid Sulfide Phase at 1473 K

The experimental results for the equilibration of molten Cu with the sulfides are listed in Table 1. The activities of CuS\(_{0.5}\) and MnS obtained by Eqs. (3) and (6) are shown in Fig. 6.

The activity of MnS in the pure liquid sulfide phase is less than unity, which might be due to the non-stoichiometric composition of copper sulfide (CuS\(_{0.48}\))\(^9\) in equilibrium with Cu.

### 3.3. Stability Diagram of the MnS–CuS\(_{0.5}\) Phases at 1473 K

In order to discuss the formation of inclusions in the \( \gamma \)-Fe phase, it is useful to refer to the stability diagram of the MnS–CuS\(_{0.5}\) phases at 1473 K against Mn and Cu contents in steel. The stability was thus estimated here, neglecting the FeS contribution in the sulfide phases due to the lack of thermodynamic data.

Possible equilibrium phases with \( \gamma \)-Fe at 1473 K are the MnS solid solution and the liquid MnS–CuS\(_{0.5}\) phase from the determined phase diagram that is shown in Fig. 5. Their formations can be deduced with the following equations:

\[
\begin{align*}
\text{2Cu(mass\% in } \gamma \text{-Fe}) + \text{S(mass\% in } \gamma \text{-Fe}) &= 2\text{CuS}_{0.5} \quad (1) \\
\end{align*}
\]

\[
\begin{align*}
\Delta G_{11}^o &= -185 \, 790 + 111 \, 118T \quad (\text{J/mol}) \quad \text{... (12)} \\
K_{11} &= \frac{\gamma_{\text{Mn}}^o}{f_{\text{Cu}}} \cdot \gamma_{\text{S}} \cdot f_{\text{S}} \cdot [\% \text{S}] \quad \text{... (13)} \\
\Delta G_{14}^o &= -263 \, 363 + 111 \, 665T \quad (\text{J/mol}) \quad \text{... (15)} \\
K_{14} &= \frac{\gamma_{\text{Mn}}^o}{f_{\text{Mn}}} \cdot \gamma_{\text{S}} \cdot f_{\text{S}} \cdot [\% \text{S}] \quad \text{... (16)}
\end{align*}
\]

The free energy changes in Eqs. (11) and (14) were derived from the thermodynamic properties of Cu\(_{13}\) S\(_{14}\) and Mn\(_{5}\) in \( \gamma \)-Fe. The activities of MnS and CuS\(_{0.5}\) were assumed to obey Raoultian and Henrian behaviors in the MnS solid solution. The activities in the liquid sulfide phase were used in the data of Fig. 6, although its non-stoichiometry at the Cu saturation does not coincide correctly with that in equilibrium with \( \gamma \)-Fe.

The activity coefficients of the components in \( \gamma \)-Fe are represented in the equations below, which contain the first-order interaction parameters for \( \gamma \)-Fe.

\[
\begin{align*}
\log f_{\text{Cu}} &= \varepsilon_{\text{Cu}}^\text{Mn} + \varepsilon_{\text{Cu}}^\text{S} + \varepsilon_{\text{Cu}}^\text{Mn} \quad \text{... (17)} \\
\log f_{\text{Mn}} &= \varepsilon_{\text{Mn}}^\text{Mn} + \varepsilon_{\text{Mn}}^\text{S} + \varepsilon_{\text{Mn}}^\text{Cu} \quad \text{... (18)} \\
\log f_{S} &= \varepsilon_{S}^\text{Cu} + \varepsilon_{S}^\text{Mn} + \varepsilon_{S}^\text{Cu} \quad \text{... (19)}
\end{align*}
\]

The interaction parameters used in the equations are listed in Table 1.

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**Table 1.** Sulfides and molten Cu compositions after equilibrium and activities of MnS and CuS\(_{0.5}\) in the liquid sulfides at 1473 K.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Sulfides composition ( X_{\text{CuS}<em>{0.48}}, X</em>{\text{MnS}} )</th>
<th>Alloy composition</th>
<th>Activities Solute (l)</th>
<th>Activities Solute (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.982 0.018</td>
<td>0.015 1.180</td>
<td>0.950 0.071</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>0.957 0.043</td>
<td>0.014 1.040</td>
<td>0.923 0.067</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>0.909 0.091</td>
<td>0.052 1.030</td>
<td>0.917 0.241</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>0.863 0.137</td>
<td>0.068 0.895</td>
<td>0.881 0.300</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>0.794 0.206</td>
<td>0.112 0.726</td>
<td>0.822 0.454</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>0.776 0.224</td>
<td>0.125 0.733</td>
<td>0.824 0.506</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>0.651 0.349</td>
<td>0.223 0.506</td>
<td>0.715 0.732</td>
<td></td>
</tr>
<tr>
<td>C1</td>
<td>1 0</td>
<td>0 1.05</td>
<td>0.924 0</td>
<td></td>
</tr>
<tr>
<td>C2</td>
<td>1 0</td>
<td>0 1.08</td>
<td>0.931 0</td>
<td></td>
</tr>
<tr>
<td>C3</td>
<td>1 0</td>
<td>0 1.09</td>
<td>0.933 0</td>
<td></td>
</tr>
<tr>
<td>MnS sat.-1</td>
<td>0.534 0.466</td>
<td>0.344 0.400</td>
<td>0.644 0.948</td>
<td></td>
</tr>
<tr>
<td>MnS sat.-2</td>
<td>0.561 0.439</td>
<td>0.340 0.405</td>
<td>0.648 0.947</td>
<td></td>
</tr>
<tr>
<td>MnS sat.-3</td>
<td>0.546 0.454</td>
<td>0.323 0.405</td>
<td>0.649 0.902</td>
<td></td>
</tr>
</tbody>
</table>

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**Fig. 6.** Activities of MnS and CuS\(_{0.5}\) in the liquid MnS–CuS\(_{0.5}\) sulfides at 1473 K. MnS sat.–1~3, saturated with molten Cu at 1473 K is CuS\(_{0.48}\).
in Table 2. $e_{\text{Cu}}^{Mn}$ and $e_{\text{Mn}}^{\text{Cu}}$ were derived from the reported thermodynamic properties of Cu$^{13)}$ and Mn$^{15)}$ in $\gamma$-Fe, respectively. The self-interaction of S was ignored because its content in $\gamma$-Fe was negligible. Although the interaction parameters between Cu and S in $\gamma$-Fe were not available, they were assumed to be negligible, considering the small value (–0.0084) of the interaction parameter of Cu and S in molten iron.$^{16)}$ As the interaction parameters between Cu and Mn in solid Fe are not available, such interaction was not taken into account in the present calculation.

Using Eqs. (13) and (16), the stability diagram of MnS–CuS$_{0.5}$ phases was calculated with iso-S content contours, as shown in Fig. 7. The stable region of the liquid MnS–CuS$_{0.5}$ inclusion has high Cu and extremely low Mn contents. Therefore, in order to decrease the Cu content in $\gamma$-Fe to an acceptable level for practical steels by inclusion formation, the CuS$_{0.5}$ activity must be decreased by the addition of other components.

### 4. Conclusions

Fundamental thermodynamic properties of the MnS–CuS$_{0.5}$ binary system have been investigated in the present work. The following results were obtained:

1. The phase diagram of the MnS–CuS$_{0.5}$ was determined by confocal scanning laser microscope observation and chemical equilibration technique. It was found to be of a simple eutectic type with mutual solid solubility of MnS and CuS$_{0.5}$.

2. Using the chemical equilibration technique, $\gamma_{\text{Mn}}^{S}$ and $e_{\text{Mn}}^{\text{Cu}}$ in molten Cu at 1473 K were determined to be 0.197±0.006 and 3.25±0.07, respectively.

3. Activities of both MnS and CuS$_{0.5}$ in the liquid sulfide phase at 1473 K were investigated by using the chemical equilibration technique, and both of them showed positive deviation from the ideality.

4. The stability diagram of MnS–CuS$_{0.5}$ phases with iso-S content contours in $\gamma$-Fe at 1473 K was calculated. The liquid MnS–CuS$_{0.5}$ inclusion was stable in the region of high Cu and extremely low Mn contents. In order to decrease the Cu content in $\gamma$-Fe to an acceptable level for practical steels by inclusion formation, the CuS$_{0.5}$ activity must be decreased by the addition of other components.

### References