Effect of Mn on Solubility of Ti-sulfide and Ti-carbosulfide in Ultra-low C Steels

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To clarify the thermodynamic stability of Ti4C2S2 and TiS in ULC Ti-added IF steels, extraction by potentiostatic electrolysis method and chemical analysis were conducted with ULC Ti-added IF steels containing various amounts of Mn and heated at various temperatures. As the results, the solubilities of Ti4C2S2 and TiS increased with an increase in Mn content. Ti4C2S2 was more stable than TiS between 950 and 1250°C. Following solubility products were obtained.

\[
\log[\text{Ti}] \cdot [\text{C}]^{0.5} \cdot [\text{S}]^{0.5} / H^{11005} = -0.392 - 7.004/T - (4.783 - 7.401/T) \cdot \text{[Mn]}
\]
\[
\log[\text{Ti}]^{2.3} \cdot [\text{S}] = -0.021 - 5.847/T - (3.360 - 5.195/T) \cdot \text{[Mn]}
\]

KEY WORDS: ultra-low C steel; Ti; sulfide; carbosulfide; Mn; solubility.

Table 1. Solubility products of Ti4C2S2 and TiS in literatures.

<table>
<thead>
<tr>
<th>No.</th>
<th>Reference</th>
<th>Ti4C2S2</th>
<th>TiS</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Liu2)</td>
<td>6.500</td>
<td>8.20</td>
</tr>
<tr>
<td>2</td>
<td>Liu2)</td>
<td>6.030</td>
<td>6.24</td>
</tr>
<tr>
<td>3</td>
<td>Subramanian5)</td>
<td>6.75</td>
<td>16550</td>
</tr>
<tr>
<td>4</td>
<td>Subramanian5)</td>
<td>12.22</td>
<td>28230</td>
</tr>
<tr>
<td>5</td>
<td>Yoshinaga6)</td>
<td>-0.780</td>
<td>-5208</td>
</tr>
<tr>
<td>6</td>
<td>Yang7)</td>
<td>7.900</td>
<td>5.43</td>
</tr>
<tr>
<td>7</td>
<td>Coppeaux8)</td>
<td>6.320</td>
<td>4.92</td>
</tr>
<tr>
<td>8</td>
<td>Iorio9)</td>
<td>5.510</td>
<td>38464</td>
</tr>
<tr>
<td>9</td>
<td>Mitsu10)</td>
<td>4.093</td>
<td>4.28</td>
</tr>
<tr>
<td>10</td>
<td>Yamashita11)</td>
<td>7.313</td>
<td>15125</td>
</tr>
</tbody>
</table>

log[\text{Ti}]^{2.3} \cdot [\text{S}] = 0.021 - 5.847/T - (3.360 - 5.195/T) \cdot \text{[Mn]}

Table 2. Chemical composition of steels for evaluation of solubility of Ti4C2S2 and TiS (mass%).

<table>
<thead>
<tr>
<th>No.</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Al</th>
<th>N</th>
<th>Ti</th>
<th>Others</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.00-0.70</td>
<td>0.253</td>
<td>1.430</td>
<td>1.670</td>
<td>0.005</td>
<td>0.005</td>
<td>0.18</td>
<td>0.67</td>
<td>0.05-0.25</td>
</tr>
<tr>
<td>2</td>
<td>100</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.12</td>
<td>-0.38</td>
</tr>
<tr>
<td>3</td>
<td>8.40</td>
<td>0.006</td>
<td>0.665</td>
<td>0.196</td>
<td>0.010</td>
<td>4.0-8</td>
<td>0.005</td>
<td>0.10</td>
<td>0.019</td>
</tr>
<tr>
<td>4</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>23.27</td>
<td>0.020</td>
<td>0.006</td>
<td>0.010</td>
<td>0.002</td>
<td>30-175</td>
<td>0.033</td>
<td>5</td>
<td>0.017</td>
</tr>
<tr>
<td>6</td>
<td>27-36</td>
<td>0.005</td>
<td>0.081</td>
<td>0.133</td>
<td>0.010</td>
<td>28-115</td>
<td>0.045</td>
<td>22</td>
<td>0.023</td>
</tr>
<tr>
<td>7</td>
<td>30-180</td>
<td>0.014</td>
<td>0.185</td>
<td>0.210</td>
<td>0.016</td>
<td>80-190</td>
<td>0.051</td>
<td>28</td>
<td>0.047</td>
</tr>
<tr>
<td>8</td>
<td>0.10-0.2</td>
<td>-</td>
<td>-</td>
<td>0.003</td>
<td>5-10</td>
<td>-</td>
<td>3</td>
<td>0.009</td>
<td>0.020</td>
</tr>
<tr>
<td>9</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>3</td>
<td>0.001</td>
<td>0.05</td>
</tr>
</tbody>
</table>

C, S, N in mass ppm, - : not available in the paper.
Table 3 shows the experimental methods. There are 4 types of procedures. The first method is the dissolution temperature measurement by transmission electron microscopic (TEM) observation with extraction replica. The second one is potentiostatic electrolysis method. The third one is diffusion couple. The last one is sulfidizing. It is very important to choose the proper etchant. Otherwise precipitates will be dissolved. Methodology for chemical analysis using electrolytically extracted residue has been discussed in elsewhere.

Recently the computer softwares and database for thermodynamic simulation have been developed. Computer simulation of precipitation in ULC Ti-stabilized steels has been done. Oikawa et al. reviewed the solubility products in the literatures in comparison with their thermodynamic calculation by CALPHAD. They concluded that Ti₄C₂S₂ is more stable than TiS and MnS. They guessed that TiS, the metastable precipitate, easily precipitates during high temperature slab reheating because of the large activation energy for nucleation of Ti₄C₂S₂. Yamashita et al. calculated solubility of Ti₄C₂S₂ by means of Thermo-Calc with the Gibbs free energy of formation of Ti₄C₂S₂ by Iorio and Garrison. Their calculation results are listed in Table 1. As the results the solubility product of Ti₄C₂S₂ was much larger than those reported previously, and that Ti₄C₂S₂ hardly precipitates in austenite of ULC Ti-added steels. However Ti₄C₂S₂ is often observed in slabs heated below 1100°C. They explained that Ti₄C₂S₂ is meta-stable but precipitates through strain induced precipitation mechanism. Thus even in the thermodynamic researchers, the stability of Ti₄C₂S₂ and TiS has not been settled.

In the present paper, solubility products of Ti₄C₂S₂ and TiS will be calculated with the chemical analysis data that was already reported. Those solubility products will be compared with the solubility products previously reported.

2. Experimental Procedure

Ultra-low-C Ti-stabilized steels containing various amount of Mn were melted in vacuum induction furnace. The chemical compositions are given in Table 4. The ingots were heated at 1200°C and then hot forged to slabs above 900°C. As shown in Fig. 1, the slabs were heated at 1250°C for 1 h and hot rolled to 6 mm thick plates in the temperature range between 900 and 1000°C, and subsequently water quenched. The hot-rolled sheets were cut and heated at various temperatures between 950 and 1250°C for 1 h in Ar atmosphere and water quenched. Some plates were heated at 1250°C for 1 h, subsequently cooled to 950°C, kept at the temperature for 1 h and water quenched.

The sulfides were separated by means of potentiostatic electrolysis method with methanol electrolyte containing 1% (m/v) salicylic acid, 4% (v/v) methyl salicylate and 1% (m/v) tetra-methyl-ammonium chloride. The S contents in the sulfides were determined by infrared absorption method after combustion in an induction or by H₂S evolution-methylene blue spectrophotometric method. The amounts of metallic elements in separated sulfides were determined by X-ray fluorescence method.

3. Experimental Results

The variation in mass fraction of S as sulfide and carbosulfide are shown in Figs. 2 - 5. In 0.06 mass% Mn steel, most of S precipitated as TiS at 1250°C as shown in Fig. 2. There remained about 10 mass ppm solute S. Ti₄C₂S₂ and MnS precipitated very little. With a decrease in reheating temperature, TiS and solute S decreased and Ti₄C₂S₂ increased. At 950°C, S as TiS became less than 10 mass ppm and most of S precipitated as Ti₄C₂S₂. In 0.18 mass% Mn steel as shown in Fig. 3 and 0.35 mass% Mn steel as shown in Fig. 4, the fraction of S in various states changed with reheating temperature almost same as that in 0.06 mass% Mn steel. Furthermore in case of reheating at 950°C, MnS precipitated more than TiS in 0.35 mass% Mn steel. In the steel containing 0.72 mass% Mn as shown in Fig. 5, MnS precipitated most and TiS precipitated very little in no rela-
tion with reheating temperature. Ti$_4$C$_2$S$_2$ increased with a decrease in reheating temperature and precipitated as much as MnS at 950°C.

4. Discussion

4.1. Solubility Products of Ti$_4$C$_2$S$_2$ and Ti$_2$S$_3$

Solubility products were calculated as followed. The differences between chemical contents and precipitates extracted by potentiostatic electrolysis method were applied to the solute S, Ti, and Mn contents. The solute C content was calculated by using S as Ti$_4$C$_2$S$_2$, supposing TiC didn’t precipitate in austenite. In the present work, all the TiS exhibited Ti/S atomic ratio of 2/3. That doesn’t mean that Ti$_2$S$_3$ precipitated but that Fe solved in TiS. Therefore solubility products of Ti$_2$S$_3$ were calculated instead of TiS. The solubility products of Ti$_4$C$_2$S$_2$ and Ti$_2$S$_3$ in the steels with various Mn contents and reheated at various temperatures were plotted in Figs. 6 and 7. Both solubility products increased with increases in reheating temperature and Mn content. If Ti/S atomic ratio was ignored and TiS solubility product was calculated, the stability order between Ti$_4$C$_2$S$_2$ and TiS would be different as shown in Fig. 8.

By using those values of solubility products, the regression analysis has been done for each steel. The results were listed in Table 5. The regression coefficients for Ti$_4$C$_2$S$_2$ and Ti$_2$S$_3$ varied with Mn content as shown in Fig. 9. The absolute values of constant “A” and the coefficient “B” decrease with an increase in Mn content for both precipitates.

According to Ohtani and Hasebe, the effect of Mn content on the solubility products can be expressed as followed.
The regression coefficients “C” and “D” give the summation of related interaction parameters.

\[
\log(Ti\%\cdot C\%\cdot S\%^{0.5}) = A + \frac{B}{T} + \left( C + \frac{D}{T} \right)\cdot Mn\% \quad (1)
\]

\[
\log(Ti\%^{2/3}\cdot S\%) = A + \frac{B}{T} + \left( C + \frac{D}{T} \right)\cdot Mn\% \quad (2)
\]

The regression coefficients “C” and “D” give the summation of related interaction parameters.

\[
W_{T_{\text{Mn}}}^{Y} + 0.5\cdot W_{\text{MnC}}^{Y} + 0.5\cdot W_{\text{MnS}}^{Y} = \frac{-5.494 \cdot R \cdot \ln(10)}{55.85} \cdot (D + C \cdot T) = -1883 \cdot (D + C \cdot T)
\]

\[
\frac{2}{3} \cdot W_{T_{\text{Mn}}}^{Y} + W_{\text{MnS}}^{Y} = \frac{-5.494 \cdot R \cdot \ln(10)}{55.85} \cdot (D + C \cdot T) = -1883 \cdot (D + C \cdot T)
\]

Several combinations of data have been used for the analysis. The results for Ti₄C₂S₂ and Ti₂S₃ are shown in Tables 6 and 7 respectively. Wₚ,ₚₙₐₜ means \( W_{T_{\text{Mn}}}^{Y} + 0.5\cdot W_{\text{MnC}}^{Y} + 0.5\cdot W_{\text{MnS}}^{Y} \) and \( 2/3 \cdot W_{T_{\text{Mn}}}^{Y} + W_{\text{MnS}}^{Y} \) respectively. As shown in the tables, the regression analysis with the data of steels containing larger Mn exhibits the smaller summation of interaction parameters.

According to Ohtani and Hillert, the interaction parameter can be evaluated from interaction coefficient by following equation.

\[
W_{AX}^{M} = RT \cdot e_{AX}^{M}
\]

The interaction coefficient of \( e_{AX}^{M} \) and \( e_{CH}^{M} \) are available in literatures. Then the interaction parameters are given as following equations.

\[
W_{\text{MnC}}^{Y} = -42.152
\]

\[
W_{\text{MnS}}^{Y} = -236.267 + 0.1064 \cdot T
\]

\( W_{T_{\text{Mn}}}^{Y} \) has not been clarified yet, but expected smaller than

**Table 6.** Results of regression analysis for Ti₄C₂S₂.

<table>
<thead>
<tr>
<th>Steel</th>
<th>Mn (mass%)</th>
<th>Ti₄C₂S₂</th>
<th>Ti₂S₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Q1-Q2</td>
<td>0.06-0.18</td>
<td>0.12</td>
<td>0.997</td>
</tr>
<tr>
<td>Q1-Q4</td>
<td>0.06-0.72</td>
<td>0.39</td>
<td>0.987</td>
</tr>
<tr>
<td>Q2-Q4</td>
<td>0.18-0.72</td>
<td>0.45</td>
<td>0.952</td>
</tr>
<tr>
<td>Q3-Q4</td>
<td>0.34-0.72</td>
<td>0.53</td>
<td>0.993</td>
</tr>
</tbody>
</table>

**Table 7.** Results of regression analysis for Ti₂S₃.

<table>
<thead>
<tr>
<th>Steel</th>
<th>Mn (mass%)</th>
<th>Ti₂S₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Q1-Q2</td>
<td>0.06-0.18</td>
<td>0.12</td>
</tr>
<tr>
<td>Q1-Q4</td>
<td>0.06-0.72</td>
<td>0.39</td>
</tr>
<tr>
<td>Q2-Q4</td>
<td>0.18-0.72</td>
<td>0.45</td>
</tr>
<tr>
<td>Q3-Q4</td>
<td>0.34-0.72</td>
<td>0.53</td>
</tr>
</tbody>
</table>
$W_{\text{MnC}}$ and $W_{\text{MnS}}$. $W_{\text{MnS}}$ is $-100.8$ and $-79.5$ kJ/mol at 1000 and 1200°C respectively. Even if the formation of Mn–C dipole were supposed, the summation of interaction parameters would not exceed 1000 kJ/mol. The binding energy of Mn–C dipole has been reported in the range between $-0.26$ and $-0.45$ eV.\textsuperscript{20–22} The interaction parameter can be given by the following equation.\textsuperscript{23}

$$W_{\text{MnC}}^\gamma = R \cdot T \cdot z' \left[ 1 - \exp \left( -\frac{\Delta E_{\text{Mn-C}}}{k_B \cdot T} \right) \right] \quad \text{.........(8)}$$

Where $-\Delta E_{\text{Mn-C}}$ is the difference in binding energy between Fe–C and Mn–C. $z'$ is the number of binding. In austenite, $z'$ is 6. Even if $-\Delta E_{\text{Mn-C}}$ were $-0.25$ eV, $W_{\text{MnC}}$ would not exceed 600 kJ/mol. The summation of interaction parameters in steels containing larger amount of Mn is closer to previously and theoretically determined value than that of low Mn steels. Then the data of high Mn added steel should be taken into account in the solubility products. This suggests that the MnS precipitation affects on the solubility of Ti$_4$C$_2$S$_2$ and Ti$_2$S$_3$.

The regression analysis was conducted with the measured solubility products in steels containing MnS more than certain minimum amount. Figure 10 shows the result. The summation of interaction parameters at 1200°C increases with an increase in minimum amount of Mn as MnS. Considering the summation of interaction parameters at higher temperatures, the data of specimens containing Mn as MnS more than 2 mass · ppm. Thus following two solubility products were obtained. The solubility product of Ti$_4$C$_2$S$_2$ is similar with that by Yoshinaga et al.\textsuperscript{6}

$$\log(\% Ti) = 0.392 - \frac{7004}{T} - \left( 4.783 - \frac{7401}{T} \right) \cdot \text{Mn\%} \quad \text{.........(9)}$$

$$\log(\% Ti^{2/3}S) = -0.021 - \frac{5847}{T} - \left( 3.360 - \frac{5195}{T} \right) \cdot \text{Mn\%} \quad \text{.........(10)}$$

By using coefficients of these solubility products, the summations of interaction parameters $W_{\text{SUM}}$ were calculated. The variations in $W_{\text{SUM}}$ with temperature were shown in Fig. 11 in comparison with $W_{\text{MnC}}$ supposing the formation of Mn–C dipole. The $W_{\text{SUM}}$ became as larger as $W_{\text{MnC}}$ at the temperature as high as 1200°C. In the lower temperature range, however the $W_{\text{SUM}}$ was much smaller than $W_{\text{MnC}}$. The reason for such large temperature dependency couldn’t be clarified in the present work.

It has often been noted that the solubility products by Yoshinaga et al.\textsuperscript{6} exhibit small temperature dependence. Such small temperature dependence seems to be due to the very low Mn content. The mechanism is remained in question.

4.2. Comparison with Previous Works

The recalculated solubility product of Ti$_4$C$_2$S$_2$ in 0.3 mass% Mn steel showed good agreement with that by Yoshinaga et al.\textsuperscript{6} For the comparison with the reported solubility product, the relationship between constant $“A”$ and coefficient $“B”$ of all the reported solubility products and present solubility products listed in Table 5 was examined in Fig. 12. There is a linear relationship between two parameters except those by Yamashita et al.\textsuperscript{11} Even the solubility product measured in stainless steel can be plotted on the correlation line. Such a relation can also be found among solubility products of TiS. The relationship between constant $“A”$ and coefficient $“B”$ can be expressed as followed.

$$A = a - b \cdot B \quad \text{.................(11)}$$

All the solubility products give the solubility products similar to “$a$” at the temperature “1/b”. Those temperature for Ti$_4$C$_2$S$_2$ and TiS are 1130 and 1250°C respectively and
Table 8. Stable phase between 1000 and 1200°C and Ti/S atomic ration in TiS.

<table>
<thead>
<tr>
<th>No</th>
<th>Reference</th>
<th>Phase</th>
<th>Ti/S</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Liu</td>
<td>Ti,C=2S2</td>
<td>NA</td>
</tr>
<tr>
<td>2</td>
<td>Liu</td>
<td>Ti,C=2S2</td>
<td>NA</td>
</tr>
<tr>
<td>3</td>
<td>Yoshinaga</td>
<td>Ti,C=2S2</td>
<td>NA</td>
</tr>
<tr>
<td>4</td>
<td>Yang</td>
<td>TiS</td>
<td>0.88</td>
</tr>
<tr>
<td>5</td>
<td>Copleaux</td>
<td>TiS</td>
<td>0.934</td>
</tr>
<tr>
<td>6</td>
<td>Meteau</td>
<td>Ti,C=2S2</td>
<td>1.0</td>
</tr>
<tr>
<td>7</td>
<td>Yamashita</td>
<td>TiS</td>
<td>NA</td>
</tr>
</tbody>
</table>

Present work Ti,C=2S2 0.67

NA: not available

correspond with the precipitation nose of each precipitates. At such temperatures the precipitates become coarse and it would be easier to identify them in no respect of analytical method. True physical meanings should be discussed in elsewhere.

The stable phase between 1000 and 1200°C are listed in Table 8. The stable phase doesn’t change in this temperature range in any works. From methodological viewpoint, the data by Yoshinaga et al.9) and Copleaux et al.9) are more reliable than the others. They used electrolytical extraction. In the present work, electrolytical extraction was also used. It is notable that Copleaux et al.9) and Yang et al.9) calculated log[Ti][S], although Ti/S atomic ration were 0.934 and 0.88 respectively. If they would recalculate the solubility products Ti,S by Iorio and Garrison9) should not have been used. But Ti,S with various amount of Fe substituting Ti. As regards Yamashita et al.,11) Gibbs free energy of formation Ti,C=2S2 by Iorio and Garrison9) can not be used.

In the commercial production of ULC Ti-stabilized steel, Ti,S precipitates when slab reheating temperature is higher than 1200°C. Ti,C=2S2 precipitates when slab reheating temperature is lower than 1100°C. Oikawa et al.13) explained by using Yamada and Niikura10) report, that Ti,C=2S2 is stable but the activation energy for nucleation is large. Therefore the meta-stable Ti,S or MnS precipitates during slab reheating at around 1200°C. As the slab reheating temperature becomes lower, Ti,C=2S2 easily nucleates due to the large free energy change. Plastic deformation also makes the nucleation easier through strain induced precipitation mechanism.

5. Conclusion

To clarify the thermodynamic stability of Ti,C=2S2 and Ti,S in ULC Ti-added IF steels, extraction by potentiostatic electrolysis method and chemical analysis were conducted with ULC Ti-added IF steels containing various amounts of Mn and heated at various temperatures. As the results, the solubilities of Ti,C=2S2 and Ti,S increased with an increase in Mn content. Ti,C=2S2 was more stable than Ti,S between 950 and 1250°C. Following solubility products were obtained.

log[Ti][C]0.5[S]0.5 = 0.392 – 7.004/T – (4.783 – 7.401/T)\* [Mn]


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The authors greatly appreciate Emeritus Professor Dr. Taiji Nishizawa for his kind and thoughtful instructions concerning thermodynamics. The authors also appreciate Dr. Shigeharu Hinotani, Dr. Yasuo Inokuma, and Mr. Joh Endo, who had worked on the original analytical research, in Sumitomo Metal Technology. The authors thank Dr. Norio Imai in Sumitomo Metals for his kind advice.

REFERENCES