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

Naomitsu MIZUI,¹⁾ Toru TAKAYAMA¹⁾ and Kazuyoshi SEKINE²⁾

1) Corporate Research & Development Laboratories, Sumitomo Metal Industries Ltd., 1-8, Fuso-cho, Amagasaki 660-0891 Japan. 2) Graduate School of Environment and Information Sciences, Yokohama National University, 79-7, Tokiwadai, Hodogaya-ku, Yokohama 240-8501 Japan.

(Received on February 6, 2008; accepted on March 31, 2008)

To clarify the thermodynamic stability of $\text{Ti}_4\text{C}_2\text{S}_2$ 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 $\text{Ti}_4\text{C}_2\text{S}_2$ and TiS increased with an increase in Mn content. $\text{Ti}_4\text{C}_2\text{S}_2$ was more stable than TiS between 950 and 1250°C. Following solubility products were obtained.

$$\log[\text{Ti}] \cdot [\text{C}]^{0.5} \cdot [\text{S}]^{0.5} = 0.392 - 7004/T - (4.783 - 7401/T) \cdot [\text{Mn}]$$

$$\log[\text{Ti}]^{2/3} \cdot [\text{S}] = -0.021 - 5847/T - (3.360 - 5195/T) \cdot [\text{Mn}]$$

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

1. Introduction

Ultra-low C (ULC) Ti-stabilized and semi-stabilized cold-rolled sheet steels have been widely applied to automotive body. Fully stabilized steel, so called Interstitial-Free (IF) steel, exhibits excellent deep drawability and is applied to deep drawn parts. Semi-stabilized steels exhibits bake-hardenability due to remained solute C and is applied to exposed panels with dent resistance. Both deep drawability and bake-hardenability are obtained by control of precipitation in the steels.¹⁾

In ULC Ti-added steels, TiN , TiS , MnS , $\text{Ti}_4\text{C}_2\text{S}_2$ and TiC precipitate. TiN is the most stable and precipitates during cooling after casting. TiC is the most unstable and precipitates after coiling in hot rolling process. As regards the thermodynamic stability of sulfides and carbosulfide, several researchers have reported empirical solubility products.^{2–10)} However there still remained uncertainty due to the variations in the chemical composition of steels used in experiments, the experimental procedures, and analytical

methods. Solubility product of $\text{Ti}_4\text{C}_2\text{S}_2$ and TiS are listed in **Table 1**. Only the solubility product by Yamashita *et al.* was simulation result by means of Thermo-Calc and reproduced from the figure in the paper.¹¹⁾ **Table 2** shows the list of experimental materials used in each work. Some used low-C steels. Not only C but also Mn and Ti contents varied. Iorio and Garrison studied on stainless steel.

Table 1. Solubility products of $\text{Ti}_4\text{C}_2\text{S}_2$ and TiS in literatures.

No.	Reference	$\text{Ti}_4\text{C}_2\text{S}_2$		TiS	
		A	B	A	B
1	Lui ²⁾	6.500	-15600	8.20	-17640
2	Lui ³⁾	6.030	-15310	6.24	-14559
3	Subramanian ⁵⁾			6.75	-16550
4	Subramanian ⁵⁾			12.22	-25230
5	Yoshinaga ⁶⁾	-0.780	-5208	-2.01	-3252
6	Yang ⁷⁾	7.900	-17045	5.43	-13975
7	Copreaux ⁸⁾	6.320	-15350	6.92	-16550
8	Iorio ⁹⁾	5.510	-14646		
9	Mitsui ¹⁰⁾	4.093	-12590	4.28	-12587
10*	Yamashita ¹¹⁾	7.313	-15125		

$$\log[\text{Ti}][\text{C}]^{0.5}[\text{S}]^{0.5}, \log[\text{Ti}][\text{S}] = A+B/T$$

Table 2. Chemical composition of steels for evaluation of solubility of $\text{Ti}_4\text{C}_2\text{S}_2$ and TiS (mass%).

No.	C	Si	Mn	P	S	Al	N	Ti	Others
1	500-720	0.253	1.430-1.670	0.005	100	0.018	67	0.05-0.25	
2	100	-	-	-	-	-	-	0.12-0.38	
3	8-40	0.006	0.066-0.196	0.010	40-80	0.005	30	0.019-0.068	
4	-	-	-	-	-	-	-	-	
5	23-27	0.020	0.006-0.010	0.002	30-175	0.033	5	0.017-0.028	
6	27-36	0.005	0.081-0.133	0.010	28-115	0.045	22	0.023-0.095	
7	30-180	0.014	0.185-0.210	0.016	80-190	0.051	28	0.047-0.204	Ni:0.06 Cr:0.03
8	0.16-0.2	-	-	0.003	5-10	-	3	0.009-0.020	Ni:10, Co:13, Cr:2, Mo:1
9	-	-	-	-	-	-	-	0.001-0.05	

C,S,N in mass ppm., - : not available in the paper.

Table 3. Experimental methods for evaluation of solubility of $\text{Ti}_4\text{C}_2\text{S}_2$ and TiS.

No.	Method	Deformation	Reheating(°C)
1	EPMA, TEM with extraction replica	Hot rolled above 820°C	1220
2	Sulfidizing in $\text{H}_2\text{S}+\text{H}_2$ gas (by Swisher ⁴⁾)	Deformation in sheet	1150-1300
3	Dissolution temperature measurement by TEM with extraction replica	Cut out from hot bands	900-1385
4	Diffusion couple		1250-1350
5	Precipitation, extraction by potentiostatic electrolysis method, and chemical analysis	Rough hot rolled, reheated at 1100°C, hot rolled above 930°C, air cooled	1000-1250
6	Dissolution temperature measurement by TEM with extraction replica	Cut out from ingot	1100-1350
7	Precipitation, extraction by potentiostatic electrolysis method, and chemical analysis	Cut out from ingot	1050-1250
8	Dissolution temperature measurement by TEM with extraction replica	Commercial processed sheet	1250-1390
9	Diffusion couple		1100-1300

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.¹²⁻¹⁴⁾

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.*¹⁵⁾ reviewed the solubility products in the literatures in comparison with their thermodynamic calculation by CALPHAD. They concluded that $\text{Ti}_4\text{C}_2\text{S}_2$ 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 $\text{Ti}_4\text{C}_2\text{S}_2$. Yamashita *et al.*¹¹⁾ calculated solubility of $\text{Ti}_4\text{C}_2\text{S}_2$ by means of Thermo-Calc with the Gibbs free energy of formation of $\text{Ti}_4\text{C}_2\text{S}_2$ by Iorio and Garrison.⁹⁾ Their calculation results are listed in Table 1. As the results the solubility product of $\text{Ti}_4\text{C}_2\text{S}_2$ was much larger than those reported previously, and that $\text{Ti}_4\text{C}_2\text{S}_2$ hardly precipitates in austenite of ULC Ti-added steels. However $\text{Ti}_4\text{C}_2\text{S}_2$ is often observed in slabs heated below 1100°C. They explained that $\text{Ti}_4\text{C}_2\text{S}_2$ is meta-stable but precipitates through strain induced precipitation mechanism. Thus even in the thermodynamic researchers, the stability of $\text{Ti}_4\text{C}_2\text{S}_2$ and TiS has not been settled.

In the present paper, solubility products of $\text{Ti}_4\text{C}_2\text{S}_2$ and TiS will be calculated with the chemical analysis data that was already reported.¹²⁾ 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

Table 4. Chemical compositions of steels (mass%).

Steel	C	Si	Mn	P	S	sol.Al	N	Ti	O
Q1	0.0024	0.001	0.06	0.008	0.0065	0.041	0.0007	0.045	0.002
Q1	0.0023	0.002	0.18	0.008	0.0067	0.041	0.0009	0.044	0.003
Q3	0.0027	0.002	0.34	0.008	0.0067	0.039	0.0008	0.046	0.002
Q4	0.0030	0.003	0.72	0.007	0.0064	0.042	0.0017	0.044	0.001

Fig. 1. Experimental procedure.

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 H_2S 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. $\text{Ti}_4\text{C}_2\text{S}_2$ and MnS precipitated very little. With a decrease in reheating temperature, TiS and solute S decreased and $\text{Ti}_4\text{C}_2\text{S}_2$ increased. At 950°C, S as TiS became less than 10 mass·ppm and most of S precipitated as $\text{Ti}_4\text{C}_2\text{S}_2$. 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-

Fig. 2. Effect of reheating temperature on fraction of sulfides in 0.06 mass% Mn steel.

Fig. 3. Effect of reheating temperature on fraction of sulfides in 0.18 mass% Mn steel.

Fig. 4. Effect of reheating temperature on fraction of sulfides in 0.34 mass% Mn steel.

Fig. 5. Effect of reheating temperature on fraction of sulfides in 0.72 mass% Mn steel.

tion with reheating temperature. $Ti_4C_2S_2$ increased with a decrease in reheating temperature and precipitated as much as MnS at 950°C.

Fig. 6. Solubility product of $Ti_4C_2S_2$.

Fig. 7. Solubility product of Ti_2S_3 .

4. Discussion

4.1. Solubility Products of $Ti_4C_2S_2$ and Ti_2S_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 $Ti_4C_2S_2$, 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_2S_3 precipitated but that Fe solved in TiS. Therefore solubility products of Ti_2S_3 were calculated instead of TiS. The solubility products of $Ti_4C_2S_2$ and Ti_2S_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 $Ti_4C_2S_2$ 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 $Ti_4C_2S_2$ and Ti_2S_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,¹⁶⁾ the effect of Mn content on the solubility products can be expressed as followed.

Fig. 8. Comparison in solubility products of TiS, $\text{Ti}_4\text{C}_2\text{S}_2$ and Ti_2S_3 in steel containing 0.34 mass% Mn and reheated at various temperatures.

Table 5. Results of regression analysis for each steel.

Steel	Mn (mass%)	$\text{Ti}_4\text{C}_2\text{S}_2$			Ti_2S_3		
		R	A	B	R	A	B
Q1	0.06	0.996	0.504	-7323	0.908	-0.038	-6259
Q2	0.18	0.997	-0.382	-5858	0.951	-0.716	-4886
Q3	0.34	0.991	-1.326	-4334	0.917	-1.454	-3697
Q4	0.72	0.997	-2.991	-1773	0.977	-2.330	-2257

$\log[\text{Ti}][\text{C}]^{0.5}[\text{S}]^{0.5}$, $\log[\text{Ti}]^{2/3}[\text{S}]=A+B/T$, R: multiple correlation coefficient

Fig. 9. Variation in regression coefficients for $\text{Ti}_4\text{C}_2\text{S}_2$ and Ti_2S_3 with Mn content.

Table 6. Results of regression analysis for $\text{Ti}_4\text{C}_2\text{S}_2$.

Steel	Mn (mass%)		Regression analysis					W_{SUM} (kJ/mol)	
	Range	Average	R	A	B	C	D	1000°C	1200°C
Q1-Q2	0.06-0.18	0.12	0.997	0.950	-8060	-7.433	12282	-5310	-2511
Q1-Q4	0.06-0.72	0.39	0.987	0.636	-7489	-5.221	8263	-3045	-1079
Q2-Q4	0.18-0.72	0.45	0.992	0.404	-7065	-4.801	7497	-2608	-800
Q3-Q4	0.34-0.72	0.53	0.993	0.173	-6642	-4.435	6824	-2219	-549

$\log[\text{Ti}][\text{C}]^{0.5}[\text{S}]^{0.5}=A+B/T+(C+D/T)[\text{Mn}]$, R: multiple correlation coefficient

Table 7. Results of regression analysis for Ti_2S_3 .

Steel	Mn (mass%)		Regression analysis					W_{SUM} (kJ/mol)	
	Range	Average	R	A	B	C	D	1000°C	1200°C
Q1-Q2	0.06-0.18	0.12	0.937	0.306	-6952	-5.718	11541	-8026	-5872
Q1-Q4	0.06-0.72	0.39	0.919	-0.045	-6144	-3.375	5792	-2816	-1545
Q2-Q4	0.18-0.72	0.45	0.952	-0.313	-5550	-2.892	4721	-1956	-867
Q3-Q4	0.34-0.72	0.53	0.944	-0.669	-4989	-2.325	3827	-1631	-755

$\log[\text{Ti}]^{2/3}[\text{S}]=A+B/T+(C+D/T)[\text{Mn}]$, R: multiple correlation coefficient

$$\log(\text{Ti}\% \cdot \text{C}\% \cdot \text{S}\%^{0.5}) \cong A + \frac{B}{T} + \left(C + \frac{D}{T}\right) \cdot \text{Mn}\% \quad \dots(1)$$

$$\log(\text{Ti}\%^{2/3} \cdot \text{S}\%) \cong A + \frac{B}{T} + \left(C + \frac{D}{T}\right) \cdot \text{Mn}\% \quad \dots(2)$$

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

$$\begin{aligned} W_{\text{TiMn}}^{\gamma} + 0.5 \cdot W_{\text{MnC}}^{\gamma} + 0.5 \cdot W_{\text{MnS}}^{\gamma} \\ \cong - \frac{5494 \cdot R \cdot \ln(10)}{55.85} \cdot (D + C \cdot T) = -1883 \cdot (D + C \cdot T) \end{aligned} \quad \dots(3)$$

$$\begin{aligned} \frac{2}{3} \cdot W_{\text{TiMn}}^{\gamma} + W_{\text{MnS}}^{\gamma} \\ \cong - \frac{5494 \cdot R \cdot \ln(10)}{55.85} \cdot (D + C \cdot T) = -1883 \cdot (D + C \cdot T) \end{aligned} \quad \dots(4)$$

Several combinations of data have been used for the analysis. The results for $\text{Ti}_4\text{C}_2\text{S}_2$ and Ti_2S_3 are shown in **Tables 6** and **7** respectively. W_{SUM} means $W_{\text{TiMn}}^{\gamma} + 0.5 \cdot W_{\text{MnC}}^{\gamma} + 0.5 \cdot W_{\text{MnS}}^{\gamma}$, and $2/3 \cdot W_{\text{TiMn}}^{\gamma} + W_{\text{MnS}}^{\gamma}$ 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,¹⁷⁾ the interaction parameter can be evaluated from interaction coefficient by following equation.

$$W_{\text{MX}}^{\gamma} = RT \cdot \varepsilon_X^{\text{M}} \quad \dots(5)$$

The interaction coefficient of $\varepsilon_{\text{C}}^{\text{Mn}}$, $\varepsilon_{\text{Mn}}^{\text{S}}$ are available in literatures.^{18,19)} Then the interaction parameters are given as following equations.

$$W_{\text{MnC}}^{\gamma} = -42.152 \quad \dots(6)$$

$$W_{\text{MnS}}^{\gamma} = -236.267 + 0.1064 \cdot T \quad \dots(7)$$

W_{TiMn}^{γ} has not been clarified yet, but expected smaller than

W_{MnC}^{γ} and W_{MnS}^{γ} . W_{MnS}^{γ} 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.^{20–22)} The interaction parameter can be given by the following equation.²³⁾

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

Where $-\Delta\epsilon_{\text{MnC}}$ 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 $-\Delta\epsilon_{\text{MnC}}$ were -0.25 eV, W_{MnC}^{γ} 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 chosen. The solute Mn content has been already taken into account in the solubility products. This suggests that the MnS precipitation affects on the solubility of $\text{Ti}_4\text{C}_2\text{S}_2$ and Ti_2S_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 $\text{Ti}_4\text{C}_2\text{S}_2$ is similar with that by Yoshinaga *et al.*⁶⁾

$$\log(\text{Ti}\% \cdot \text{C}\%^{0.5} \cdot \text{S}\%^{0.5}) \cong 0.392 - \frac{7004}{T} - \left(4.783 - \frac{7401}{T} \right) \cdot \text{Mn}\% \dots\dots\dots(9)$$

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

By using coefficients of these solubility products, the summations of interaction parameters W_{SUM} were calcu-

Fig. 10. Variation in summation of interaction parameters at 1200°C with minimum precipitating Mn.

lated. The variations in W_{SUM} with temperature were shown in **Fig. 11** in comparison with W_{MnC}^{γ} supposing the formation of Mn–C dipole. The W_{SUM} became as large as W_{MnC}^{γ} at the temperature as high as 1200°C . In the lower temperature range, however the W_{SUM} was much smaller than W_{MnC}^{γ} . 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.*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 $\text{Ti}_4\text{C}_2\text{S}_2$ in 0.3 mass% Mn steel showed good agreement with that by Yoshinaga *et al.*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.*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 fol-

$$A = a - b \cdot B \dots\dots\dots(11)$$

All the solubility products give the solubility products similar to “a” at the temperature “ $1/b$ ”. Those temperature for $\text{Ti}_4\text{C}_2\text{S}_2$ and TiS are 1130 and 1250°C respectively and

Fig. 11. Variation in summation of interaction parameters with temperature.

Fig. 12. Relationship between coefficient and constant in solubility products of $\text{Ti}_4\text{C}_2\text{S}_2$.

Table 8. Stable phase between 1 000 and 1 200°C and Ti/S atomic ration in TiS.

No.	Reference	Phase	Ti/S
1	Lui ²⁾	Ti ₄ C ₂ S ₂	NA
2	Lui ³⁾	Ti ₄ C ₂ S ₂	NA
5	Yoshinaga ⁶⁾	Ti ₄ C ₂ S ₂	NA
6	Yang ⁷⁾	TiS	0.88
7	Copreaux ⁸⁾	TiS	0.934
9	Mitsui ¹⁰⁾	Ti ₄ C ₂ S ₂	1.0
10	Yamashita ¹¹⁾	TiS	NA
	Present work	Ti ₄ C ₂ S ₂	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 1 000 and 1 200°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.*⁶⁾ and Copreaux *et al.*⁸⁾ are more reliable than the others. They used electrolytical extraction. In the present work, electrolytical extraction was also used. It is notable that Copreaux *et al.*⁸⁾ and Yang *et al.*⁷⁾ calculated $\log[\text{Ti}][\text{S}]$, although Ti/S atomic ration were 0.934 and 0.88 respectively. If they would recalculate the solubility products in consideration with Ti/S atomic ratio, TiS might be a metastable phase. Sanagi *et al.*²⁴⁾ reported Ti/S atomic ratio varied with reheating temperature. Dupuis *et al.*²⁵⁾ also pointed out, that the stoichiometries of Ti-carbosulfide is always reported as Ti₄C₂S₂. However Ti/S atomic ratio of Ti-sulfide varied, 0.67,¹²⁾ 0.85,²⁵⁾ 0.88,⁷⁾ 0.89,²⁶⁾ 1.3.²⁷⁾ These Ti_xS seem to be not different phases but TiS with various amount of Fe substituting Ti. As regards Yamashita *et al.*,¹¹⁾ Gibbs free energy of formation Ti₄C₂S₂ by Iorio and Garrison⁹⁾ should not have been used.

In the commercial production of ULC Ti-stabilized steel, TiS precipitates when slab reheating temperature is higher than 1 200°C. Ti₄C₂S₂ precipitates when slab reheating temperature is lower than 1 100°C. Oikawa *et al.*¹⁵⁾ explained by using Yamada and Niikura²⁸⁾ report, that Ti₄C₂S₂ is stable but the activation energy for nucleation is large. Therefore the meta-stable TiS or MnS precipitates during slab reheating at around 1 200°C. As the slab reheating temperature becomes lower, Ti₄C₂S₂ 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 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 1 250°C. Following solubility products were obtained.

$$\log[\text{Ti}][\text{C}]^{0.5}[\text{S}]^{0.5}=0.392-7\,004/T-(4.783-7\,401/T^{\#})\cdot[\text{Mn}]$$

$$\log[\text{Ti}]^{2/3}[\text{S}]=-0.021-5\,847/T-(3.360-5\,195/T^{\#})\cdot[\text{Mn}]$$

Acknowledgements

The authors greatly appreciate Emeritus Professor at Tohoku University 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

- 1) N. Mizui: Proc. Int. Symp. "Modern LC and ULC Sheet Steels for Cold Forming: Processing and Properties", ed. by W. Bleck, Verlag Mainz, Aachen, Germany, (1998), 169.
- 2) W. J. Liu, S. Yue and J. J. Jonas: *Metall. Mater. Trans. A*, **20A** (1989), 1907.
- 3) W. J. Liu, J. J. Jonas, D. Bouchard and C. W. Bale: *ISIJ Int.*, **30** (1990), 985.
- 4) J. H. Swisher: *Trans. Metall. Soc. AIME*, **242** (1968), 2433.
- 5) S. V. Subramanian, M. Prikryl, A. Ulabhaje and K. Balasubramanian: Proc. Int. Symp. Interstitial Free Steel Sheet, ed. by A. J. DeArdo, Canadian Inst. Mining Metall. Petro., Montreal, (1991), 15.
- 6) N. Yoshinaga, K. Ushioda, S. Akamatsu and O. Akisue: *ISIJ Int.*, **34** (1994), 24.
- 7) X. Yang, J. Dilewijns, Y. Houbaert, D. Vanderschueren and C. Standaert: *ISIJ Int.*, **36** (1996), 1286.
- 8) J. Copreaux, H. Gaye, J. Henry and S. Lanteri: ECSC Report, EUR 17806 FR, (1997).
- 9) L. E. Iorio and M. Garrison, Jr.: *ISIJ Int.*, **42** (2002), 545.
- 10) H. Mitsui, K. Oikawa, I. Oonuma, R. Kainuma and K. Ishida: *CAMP-ISIJ*, **17** (2004), 1275.
- 11) T. Yamashita, K. Okuda, E. Yasuhara and K. Satoh: *Tetsu-to-Hagane*, **93** (2007), 538.
- 12) S. Hinotani, T. Takayama, N. Mizui, J. Endo and Y. Inokuma: *ISIJ Int.*, **34** (1994), 17.
- 13) Y. Ishiguri and K. Sato: *Mater. Trans. JIM*, **37** (1996), 643.
- 14) T. Ichioka, Y. Sukenobu, Y. Kurakake, M. Aoki and Y. Higo: *Nishin Steel Tech. Rep.*, **79** (1999), 18.
- 15) K. Oikawa, H. Mitsui and K. Ishida: *Mater. Sci. Forum*, **500-501** (2005), 711.
- 16) H. Ohtani and M. Hasebe: *Bull. Iron Steel Inst. Jpn.*, **11** (2006), 457.
- 17) H. Ohtani and M. Hillert: *Calphad*, **15** (1991), 25.
- 18) T. Wada, H. Wada, J. F. Elliott and J. Chipman: *Metall. Mater. Trans.*, **3** (1972), 2865.
- 19) E. J. Turkdogan, S. Ignatowicz and J. Pearson: *J. Iron Steel Inst.*, **180** (1955), 349.
- 20) H. Abe, T. Suzuki and S. Okada: *Trans. Iron Steel Inst. Jpn.*, **25** (1984), 215.
- 21) K. Tagashira, N. Sumita and H. Hayakawa: *Mater. Trans. JIM*, **30** (1989), 10.
- 22) V. Massardier, E. Le Patezour, M. Soler and J. Merlin: *Metall. Mater. Trans. A*, **36A** (2005), 1745.
- 23) C. H. Plupis and J. F. Elliott: *Acta Metall.*, **14** (1966), 1019.
- 24) S. Sanagi, K. Kawasaki and T. Kawano: *CAMP-ISIJ*, **2** (1989), 2015.
- 25) G. Dupuis, R. A. Hubert and R. Tailard: 40th MWSP Conf. Proc., ISS, Warrendale, PA, (1998), 117.
- 26) M. Prikryl, Y. P. Lin and S. V. Subramanian: *Scr. Metall.*, **24** (1990), 375.
- 27) O. Hamart and S. Lantei: 38th MWSP Cong., Vol. 34, ISS, Warrendale, PA, (1997), 431.
- 28) K. Yamada and M. Niikura: *Tetsu-to-Hagane*, **81** (1995), 197.