Characterization of Ti Carbosulfide Precipitation in Ti Microalloyed Steels

W.J. LIU, S. YUE, and J.J. JONAS

The morphology and composition of the Ti carbosulfides observed in a family of steels containing 0.05 to 0.25 wt pct Ti were determined using optical and electron microscopy, electron microprobe analysis, and energy-dispersive X-ray (EDX) and secondary ion mass spectrometer (SIMS) techniques. It is demonstrated that the Ti carbosulfide phase has a Ti:S mole fraction ratio of 2:1 and contains an appreciable level of carbon, its identity being Ti₄C₂S₂. The solubility product of Ti₄C₂S₂ in austenite is derived to be log [Ti] [C]₀.₅[S]₀.₅ = -15,600/T + 6.50 and that of TiS to be log [Ti] [S] = -17,640/T + 8.20. The former lies between the values for TiN and TiC, whereas the latter is more soluble than TiC. Stringer inclusions consisting of globular Ti₄C₂S₂ surrounded by elongated MnS were observed in the steels with 0.05 to 0.18 wt pct Ti. The volume fraction of the stringers is shown to be related to the sulfur partition coefficient through an empirical power law function.

I. INTRODUCTION

It has long been recognized that a variety of important properties of strip and plate steel products, such as cold formability and toughness anisotropy, can be drastically improved by Ti addition. The striking effect of Ti on steel properties has been attributed to the formation of Ti carbosulfide (Ti₄C₂S₂), which remains undeformed during hot rolling due to its high hardness at elevated temperatures. Since Ti₄C₂S₂ is more stable than MnS in iron-based alloys, the formation of MnS, which is usually deformed into undesirably long stringers during hot rolling, is restrained by the addition of Ti to the steel. Furthermore, in recent investigations carried out in Japan, it has been shown that the formation of Ti₄C₂S₂ plays an important role in improving the deep drawability of interstitial-free (IF) steels, although the mechanisms responsible for this effect have not yet been identified. However, in spite of the importance of this phase in steel products, little information has been published to date on its solubility and precipitation behavior in the presence of Mn.

Ti₄C₂S₂ was first reported by Kudielka and Rohde to possess a hexagonal structure of space group D₆h-P6₃/mmc with lattice parameters a = 3.21 Å and c = 11.20 Å. Later investigations of the carbosulfide phase found in a number of steel grades and in the nickel-base superalloys led to similar values for these quantities. The excellent agreement regarding the lattice parameters of Ti₄C₂S₂ found in a wide range of alloy systems suggests that the limits of composition of this phase are not wide and that Ti₄C₂S₂ forms as a stoichiometric or near-stoichiometric compound rather than as a compound with variable stoichiometry of the type TiₓCᵧS₁₋ₓ. In practice, Ti₄C₂S₂ is often confused with Ti₂S, because the diffraction patterns of the two phases are nearly identical. However, in a recent paper, Ball has presented evidence that the phase initially identified as Ti₂S is, in fact, Ti carbosulfide, and that Ti₂S does not exist in steels. Although the above controversy could be clarified by direct composition measurements, most previous investigations were carried out on extracted particles, which generally contain TiN, TiC, and other precipitates, leading to some uncertainty in the analyses. Additionally, it is difficult to detect carbon by microanalysis, so that the particle composition is frequently incompletely known. In comparison with the knowledge of the crystal structure, still less attention has been paid to the solubility of Ti₄C₂S₂, except that its Gibbs free energy of formation in austenite has been estimated in a recent study.

In the present study, we have employed SIMS and microprobe analysis to establish the composition of the Ti sulfide formed in a series of Ti-bearing high-strength low-alloy (HSLA) steels. This is identified as the Ti carbosulfide Ti₄C₂S₂. The S partition coefficients between the carbosulfide and MnS were also measured. By this means, and on the basis of the free energy of formation of Ti₄C₂S₂ proposed previously, the solubility product for Ti carbosulfide in high-temperature austenite is derived and presented.

II. EXPERIMENTAL PROCEDURE

A. Experimental Materials

Four Ti-bearing steels were studied with a base composition modeled fairly closely on conventional HSLA steels. The chemical compositions of these steels are listed in Table I. The materials were cast into rectangular ingots of approximate dimensions 125 × 150 × 225 mm. They were reheated to 1220 °C and soaked at this temperature for 2 hours prior to being hot rolled in 20 passes to a thickness of 13 mm with a finishing temperature of about 820 °C. For metallographic purposes, 10 × 10 × 13-mm samples were cut from the central regions of the as-rolled plates.
Table I. Chemical Compositions in Weight Percent of the Steels Tested

<table>
<thead>
<tr>
<th>Steel Ti</th>
<th>C</th>
<th>N</th>
<th>Mn</th>
<th>Si</th>
<th>Al</th>
<th>S</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05 pct Ti</td>
<td>0.05</td>
<td>0.072</td>
<td>0.0052</td>
<td>1.52</td>
<td>0.24</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>0.11 pct Ti</td>
<td>0.115</td>
<td>0.060</td>
<td>0.0062</td>
<td>1.67</td>
<td>0.2</td>
<td>0.03</td>
<td>0.01</td>
</tr>
<tr>
<td>0.18 pct Ti</td>
<td>0.18</td>
<td>0.075</td>
<td>0.0084</td>
<td>1.51</td>
<td>0.3</td>
<td>0.02</td>
<td>0.01</td>
</tr>
<tr>
<td>0.25 pct Ti</td>
<td>0.25</td>
<td>0.050</td>
<td>0.0070</td>
<td>1.43</td>
<td>0.27</td>
<td>0.01</td>
<td>0.01</td>
</tr>
</tbody>
</table>

B. Morphology and Volume Fraction Measurements

Both optical and scanning electron microscopy (SEM) were carried out to quantify the size and volume fraction of the large sulfide stringers. Longitudinal sections of the rolled plates were polished for observation and microanalysis purposes. The volume fraction of stringers was estimated from measurements of up to 30 stringers in 20 fields of view which were randomly selected.

The Ti-rich sulfide particles, which were not strung out but were small and round, were examined in extraction replicas and thin foils using a JEOL-100 CX scanning transmission electron microscope. To prepare the extraction replicas, the samples were lightly etched in 3 pct nital after polishing, and thin carbon layers were deposited on their surfaces using a vacuum evaporator. The extraction replicas were released by electropolishing in a solution of 10 pct perchloric acid, 10 pct butanol, 10 pct distilled water, and 70 pct ethanol. The thin foils were prepared by jet electropolishing 3-mm disks at -20 °C in the same solution.

C. Microanalysis

Chemical microanalysis of the large elongated sulfide inclusions was carried out on a Camebax electron microprobe using the wavelength dispersive method. The raw data were ZAF corrected (i.e., the X-ray intensities were normalized for atomic number (Z), absorption (A), and fluorescence (F) effects) with Cameca software to obtain quantitative elemental values. Since most of the stringers analyzed were <1 μm thick, a significant fraction of the X-rays generated by the electron beam originated in the regions surrounding the particles. To compensate for this "matrix effect," the microanalysis data were corrected using the following relationships:

\[
X_{P} = X_{S} / \beta \tag{1}
\]

\[
X_{Ti} = (X_{Ti}^{S} - \alpha X_{P}^{S}) / \beta \tag{2}
\]

\[
X_{Mn}^{S} = (X_{Mn}^{S} - \alpha X_{P}^{S}) / \beta \tag{3}
\]

where

\[
\alpha = X_{P}^{S} / X_{P}^{M} \tag{4}
\]

\[
\beta = 1 - \alpha \tag{5}
\]

In these equations, \(X_{P}^{S}\) is the atom fraction of element \(i\) (\(i = S, Ti, Mn, \text{ and Fe}\)) in the sulfide inclusion, \(X_{P}^{S}\) is the atom fraction of \(i\) as measured in the volume containing the particle (i.e., the raw data), and \(X_{P}^{M}\) is the measured atom fraction of \(i\) in the matrix. The detailed derivation of the above correction equations is given in the Appendix.

To investigate the extent of composition heterogeneity in the stringers, X-ray maps were generated on a JEOL scanning electron microscope fitted with a TRACOR NORTHERN* energy dispersive analytical system and TRACOR NORTHERN image processing software. The compositions of the small globular sulfide particles contained in the extraction replicas were investigated with the aid of a PGT system IV EDX spectrometer attached to the TEM/STEM microscope. Secondary ion mass spectrometer analysis was performed on a Cameca IMS 3F instrument using 14.5 keV \(O^{+}\) primary ions with a beam diameter of about 100 μm. Both positively and negatively charged secondary ions of C, S, and Ti emitted from the sample surface were used to produce the mass-resolved ion images. The lateral resolution of this instrument in the direct image mode is 0.5 μm.

III. RESULTS

A. Morphology of the Sulfide Inclusions

Typical inclusion morphologies are illustrated in Figures 1(a) through (d), from which the composition heterogeneities found in the four Ti steels can be readily seen. It is evident that both the morphology and the composition of the inclusions are nonuniform, and that these are significantly influenced by the Ti concentration in the steel. Stringer inclusions were found in the 0.05, 0.11, and 0.18 pct steels, which are rich in Mn, S, and Ti, as shown in Figures 1(a) through (c). However, only globular sulfides, in which no Mn was detected, were observed in the 0.25 pct Ti steel (Figure 1(d)). In the three lower Ti steels, Ti-rich globules were often observed along the stringers; as the Ti concentration was increased, the number and size of the globules increased. The stringers found in the 0.18 pct Ti steel, for example, are appreciably distorted due to the presence of an increased frequency of large round particles. The above observations indicate that the morphology of the sulfide inclusions is strongly modified by the addition of Ti.

In addition to the large stringers and globular particles, electron microscopy also revealed the presence of small round sulfide precipitates (<1 μm in diameter) in all the Ti steels examined. Strong Ti and S peaks were always obtained when the small particles were analyzed by EDX. Some typical small sulfide precipitates are shown in Figures 2(a) and (b), together with the X-ray spectrum taken from the particle shown in Figure 2(b) and (c). Two features should be noted: (1) there is no Mn peak in the X-ray spectrum; and (2) the Ti peak is approximately two times higher than that of the S. This observation suggests that the small precipitates are nearly pure...
Fig. 1—Scanning electron microscope images and EDX X-ray maps for Mn, S, and Ti for the steels containing (a) 0.05, (b) 0.11, (c) 0.18, and (d) 0.25 pct Ti. The morphologies of the large sulfide inclusions can be readily seen, as well as the composition inhomogeneities within them.

Ti sulfides or carbosulfides in which the Ti:S ratio is close to 2:1.

The volume fraction of stringers (denoted as $V_s$) was determined by quantitative microscopy, and the results are listed in Table II. It can be seen that as the Ti level is increased from 0.05 to 0.25 pct, $V_s$ is reduced from $5 \times 10^{-4}$ to zero. The stringer morphology results from the plastic deformation of MnS during hot rolling, as the latter has a lower flow strength than the matrix at the rolling temperatures.\(^{112}\) By contrast, the strength of the titanium sulfide or carbosulfide is so high that these compounds remain essentially undeformed during hot rolling of such steels.

B. Chemical Composition of the Large Sulfide Particles

The average chemical composition of each sulfide inclusion (i.e., of the stringers as well as of the larger globular particles) was estimated by performing point analyses at several points and then averaging the results. The measured and corrected mean concentrations of the respective elements are given in Table III for the particles selected. The concentrations were corrected by employing Eqs. [1] through [5], which are derived in the Appendix.

In order to determine the chemical formula of the Ti-rich particles, the corrected concentrations of Mn, S, and Ti in each particle given in Table III are presented in Figure 3 in terms of the difference between the Mn and S concentrations plotted against the Ti concentration. It is evident that the data fit well a straight line with a slope of 1/2. If the MnS contained in the composite particles is assumed to be stoichiometric, the slope of the relationship displayed in Figure 3 indicates that the Ti sulfide constituent in the mixed sulfide particles has a Ti:S mole fraction ratio of 2:1. This is in good agreement with the X-ray spectra obtained from the small round Ti-rich
sulfide particles (Figure 2(c)). The Ti sulfide observed in the present steels can therefore be identified as either $\text{T}_2\text{S}$ or $\text{T}_4\text{C}_2\text{S}_2$.

Because of the lack of a light element detector on the microprobe used in the current work, the carbon content of the particles could not be determined simultaneously. Therefore, SIMS analyses were subsequently carried out to test for the presence of C in the Ti-rich sulfides. A typical set of ion micrographs ($^{12}\text{C}^+$, $^{33}\text{S}^+$, and $^{48}\text{Ti}^+$) taken from a Ti-rich sulfide particle in the 0.18 pct Ti

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**Table II. Volume Fraction of Stringers ($V_s$) Determined in the Four Ti Steels**

<table>
<thead>
<tr>
<th>Steel</th>
<th>$V_s \times 10^4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05 pct Ti</td>
<td>5.0</td>
</tr>
<tr>
<td>0.11 pct Ti</td>
<td>1.3</td>
</tr>
<tr>
<td>0.18 pct Ti</td>
<td>0.7</td>
</tr>
<tr>
<td>0.25 pct Ti</td>
<td>0.0</td>
</tr>
</tbody>
</table>

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**Table III. Measured and Corrected Mean Concentrations of Mn, S, and Ti in Selected Inclusions in the Four Ti Steels**

<table>
<thead>
<tr>
<th>Steel</th>
<th>Inclusion Number</th>
<th>Measured Mole Fraction $\times 10^2$</th>
<th>Corrected Mole Fraction $\times 10^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$X_{Fe}^0$</td>
<td>$X_{S}^0$</td>
<td>$X_{Ti}^0$</td>
</tr>
<tr>
<td>0.05 pct Ti</td>
<td>1</td>
<td>77.27</td>
<td>13.14</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>90.07</td>
<td>4.50</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>82.81</td>
<td>7.73</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>65.94</td>
<td>16.03</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>77.54</td>
<td>10.03</td>
</tr>
<tr>
<td>0.11 pct Ti</td>
<td>1</td>
<td>63.88</td>
<td>12.03</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>65.31</td>
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<td></td>
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<td>56.59</td>
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<tr>
<td></td>
<td>4</td>
<td>63.10</td>
<td>14.38</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>67.58</td>
<td>15.15</td>
</tr>
<tr>
<td>0.18 pct Ti</td>
<td>1</td>
<td>60.78</td>
<td>13.28</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>63.77</td>
<td>11.99</td>
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<tr>
<td></td>
<td>3</td>
<td>79.12</td>
<td>6.37</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>54.01</td>
<td>19.93</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>68.19</td>
<td>14.17</td>
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<tr>
<td></td>
<td>6</td>
<td>70.69</td>
<td>9.76</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>56.10</td>
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<td>63.65</td>
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</tr>
<tr>
<td></td>
<td>9</td>
<td>56.69</td>
<td>15.08</td>
</tr>
<tr>
<td>0.25 pct Ti</td>
<td>1</td>
<td>89.58</td>
<td>2.96</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>62.83</td>
<td>11.37</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>88.19</td>
<td>3.98</td>
</tr>
</tbody>
</table>
IV. DISCUSSION

A. Sulfur Partitioning between MnS and Ti₄C₂S₂

As shown in Figure 1, the stringers observed in the present Ti steels consist of mixtures of MnS and Ti₄C₂S₂ inclusions. Thus, the mole fraction ratio of Ti to Mn detected in the stringers can be expressed as

\[ Y = \frac{X_{Ti}^p}{X_{Mn}^p} = \frac{2X_{S}^ti}{X_{S}^mn} \]  \[6\]

Here, \(X_{Ti}^p\) and \(X_{Mn}^p\) are, respectively, the mole fractions of S combined with Ti and with Mn in a stringer particle. Furthermore, defining \(X_{S}^s\) as the overall mole fraction of S in the steel, \(X_{S}^i\) as the mole fraction of S contained in the stringer, and \(X_{S}^f\) as the mole fraction of S contained in the isolated Ti carbosulfides, we have

\[ X_{S}^0 = X_{S}^i + X_{S}^f = X_{S}^ti + X_{S}^mn + X_{S}^f \]  \[7\]

The partition coefficient of S between Ti₄C₂S₂ and MnS is defined as

\[ P_c = \frac{(X_{Ti}^s + X_{S}^s)/X_{S}^s}{X_{S}^f} \]  \[8\]


\[ P_c = (0.5Y + 1)(X_{S}^0/X_{S}^s) - 1 \]

where \([S]_0\) and \([S]_s\) are the weight percentages of S contained in the steel and combined with the stringers, respectively. The latter was determined from the following equation:

\[ [S]_s = \frac{f_S V_S \rho_S}{[(1 - V_S)\rho_{Fe} + V_S \rho_S]} \]  \[10\]

where \(\rho_S\) and \(\rho_{Fe}\) are the stringer and iron matrix densities, and \(f_S\) is the fractional weight of S in the stringer. It can be deduced that

\[ \rho_S = \left(\frac{1}{4} YZ_{Ti_4C_2S_2} + Z_{MnS}\right)/\left(\frac{1}{4} YV_{Ti_4C_2S_2} + V_{MnS}\right) \]  \[11\]

and that

\[ f_S = \frac{Z_{S} \left(1 + \frac{1}{2} Y\right)/\left(\frac{1}{4} YZ_{Ti_4C_2S_2} + Z_{MnS}\right)}{25 \mu m} \]  \[12\]

where \(Z_i\) and \(V_i\) are the atomic/molecular weight and molar volume of element/compound \(i\); their values are
given in Table IV. Using Eqs. [6] through [12], the values of [S]s and P, were calculated, and the results are summarized in Table V.

It can be seen that the sulfur partition coefficient between Ti4C2S2 and MnS depends strongly on the Ti concentration in the steel. The value of P, increases from 0.09 to 26.7 as the Ti level is increased from 0.05 to 0.18 pct. It is important to note that the samples used in this study were prepared from steels which had been soaked at 1220 °C for 2 hours prior to rolling. Due to the limitations of the electron microprobe employed, the small fresh particles precipitated during hot rolling could not be analyzed. As a result, the P, coefficients determined in this study are associated with the particles remaining undissolved at the initial temperature of 1220 °C.

B. Solubility Product of Ti4C2S2 in Austenite

In a recent study, the Gibbs free energy of formation of Ti4C2S2 in austenite was estimated from the P, values described above with the aid of a thermodynamic calculation of multiphase equilibria at 1220 °C in the steels in question. The numerical result can be represented as follows:

\[ \Delta G_{\text{Ti4C2S2}} / RT = -146,744 / T + 27.78 \]  \[ \text{(13)} \]

Considering the equilibrium between Ti4C2S2 and the austenite, we have

\[ \Delta G_{\text{Ti4C2S2}} / RT = 4 \ln a_{\text{Ti}} + 2 \ln a_{\text{C}} + 2 \ln a_{\text{S}} \]

\[ = 4 \ln X_{\text{Ti}} + 2 \ln X_{\text{C}} + 2 \ln X_{\text{S}} \quad \text{(14)} \]

where a, and X, are, respectively, the activity and mole fraction of element i (i = Ti, C, and S) in austenite. By expressing Eq. (14) in terms of [i] (weight percent of element i), the solubility product (K) of Ti4C2S2 in austenite can be written as

\[ \log K = \log [\text{Ti}]^4[\text{C}]^2[\text{S}]^2 = -62,400 / T + 26.01 \] \[ \text{(15)} \]

or

\[ \log K = \log [\text{Ti}]^5[\text{C}]^3[\text{S}]^5 = -15,600 / T + 6.50 \] \[ \text{(16)} \]

With the aid of either Eq. (15) or (16), the solubility of Ti4C2S2 in austenite at a given temperature can be represented as shown in Figure 5(a) in the form of a three-dimensional surface (for 1220 °C). This graph can explain why TiS* is often observed in IF steels, but rarely in conventional Ti-bearing microalloyed steels. The main difference between the IF and microalloyed steels lies in their carbon concentrations; the C level in a typical IF steel is usually one order of magnitude lower than in a microalloyed steel. As can be seen in Figure 5(b), because of its lower C concentration, the solubility of Ti4C2S2 in an IF steel is significantly higher than in conventional microalloyed austenite. As a result, more solute Ti and S are released from the Ti carbosulfide, leading to the increased possibility of forming TiS in the IF steels.

The temperature dependence of the solubility product of Ti4C2S2 in austenite (Eq. [16]) evaluated in this study is presented in Figure 6, together with literature data for TiN, TiC, and MnS. The solubility product for TiS was calculated from the free energy relationship \( \Delta G_{\text{TiS}} / RT = -40,580 / T + 10.40 \) derived in a recent study, which is based on the solubility data measured in a Fe-S-Ti system and reported by Swisher; this can be expressed as

\[ \log K = \log [\text{Ti}] [\text{S}] = -17,640 / T + 8.20 \] \[ \text{(17)} \]

The comparison shows that the solubility products of both Ti4C2S2 and TiS lie between the values for TiN and TiC in the austenite temperature range. This is in agreement with the precipitation sequence often observed in Ti steels.

C. Mutual Solubility of Ti4C2S2 and MnS

In the present study, most of the stringer inclusions were found to be composed of Ti4C2S2 globules surrounded by MnS (Figure 1). Similar morphologies were also observed by other investigators. This type of structure indicates that the stringers are likely to be formed by the nucleation of MnS on already existing Ti4C2S2. Thus, it seems reasonable to assume that there is only limited mutual solubility of Ti4C2S2 and MnS during their coprecipitation. This assumption is supported by the thermodynamic analysis carried out for the present Ti steels. The limited mutual solubility between Ti4C2S2 and MnS is probably due to a structural difference. MnS in steel has a cubic crystal lattice and belongs to space group Fm3m with the parameter a = 5.226 Å, while Ti4C2S2 has a hexagonal structure.

*It has generally been agreed that the most likely sulfide precipitates in Ti-bearing steels are TiS, Ti2S, and Ti4C2S2. However, there is limited evidence that the phase initially identified as Ti2S is Ti4C2S2, and that Ti2S does not exist in steels. Thus, when Ti4C2S2 is absent, the sulfide that is likely to form is TiS and not Ti2S; it can easily be differentiated from TiS or Ti4C2S2 by testing for the Ti:S ratio.
D. Relation between Volume Fraction of Stringers and Sulfur Partition Coefficient

Stringer inclusions are formed during hot rolling as a result of the extension of MnS along the rolling direction. Such an inclusion shape is harmful to the cold formability and isotropy of toughness properties of strip and plate steel products. The size and shape of the sulfide inclusions can be modified by alloying with elements of high sulfur affinity, such as Ca, Mg, Ti, Zr, and the rare earths. The present results indicate that the volume fraction of stringers depends sensitively on the Ti concentration in the steel and, therefore, on the sulfur partition coefficient. As can be seen from Tables II and V, the 0.05 pct Ti steel contains a stringer volume fraction of $5.0 \times 10^{-4}$ and has a sulfur partition coefficient of 0.09. As the Ti level is increased to 0.18 pct, $V_s$ decreases to $0.7 \times 10^{-4}$, and $P_c$ increases to 26.7. Therefore, it is of interest at this point to establish a quantitative relationship between the observed stringer volume fraction and $P_c$. For this purpose, we write that

$$V_s = V_m f(P_c) \quad [18]$$

where $V_m$ is the volume fraction of MnS (or of the stringers) when $P_c = 0$ (in other words, when all the sulfur is combined as MnS); this is approximately equal to $0.053[S]^{0.12}$ where $[S]$ is the weight percent of S in the steel. When the $P_c$ function is of the form $f(P_c) = (1 + AP_c)^{-n}$, Eq. [18] fulfills the required boundary conditions; i.e., when $P_c = 0$, $V_s = V_m$, and when $P_c = \infty$, $V_s = 0$. By best fitting the stringer volume fractions (in terms of $V_s/V_m$) determined in the present study to the $P_c$ function given above, the constants $A$ and $n$ were evaluated to be 3.34 and 0.45, respectively. Thus, Eq. [18] can be rewritten as

$$V_s = 0.053[S] \left(1 + 3.34 P_c\right)^{-0.45} \quad [19]$$
As an example of the application of Eq. [19] to a realistic problem, a calculation was carried out over the Ti level from 0.025 to 0.3 wt pct for the base composition of the 0.05 pct Ti steel. The dependence of \( P_c \) on Ti concentration was first predicted using the thermodynamic model described in Reference 10. The results are presented in Figure 7. It can be seen that as the Ti concentration is increased, \( P_c \) increases and \( V_s \) decreases. It is of interest that the volume fraction of stringers remains at its maximum value of \( 5.3 \times 10^{-4} \) until the Ti level attains 0.02 pct, which is slightly higher than the stoichiometric concentration required for the formation of TiN, i.e., 0.018 pct, when this is the only Ti precipitate that forms. When the Ti concentration is increased further, \( V_s \) starts to decrease slowly at first and then more quickly after the Ti level exceeds 0.035 pct. Finally, when the Ti concentration is increased to more than 0.1 pct, at which point \( V_s \) has been reduced to about 20 pct of its original level, the rate of reduction of \( V_s \) decreases again significantly. Thus, it can be concluded that for the purpose of sulfide shape control, the optimum level of Ti addition in the presence of about 1.5 pct Mn is around five to six times that required to tie up the N present in the form of TiN. Titanium levels lower than double the stoichiometric concentration necessary to form TiN cannot actually affect sulfide shape. On the other hand, Ti additions of more than the optimum concentration (0.1 pct in this case) can only reduce the \( V_s \) level at a much slower rate.

V. CONCLUSIONS

1. The Ti-rich sulfide phase observed in the present Ti-bearing HSLA steels was examined using an electron microprobe and EDX and SIMS analyses. It has a Ti:S mole fraction ratio of 2:1 and contains an appreciable level of carbon. As C does not appear to have appreciable solid solubility in Ti2S, this phase can be identified as Ti4C2S2.

2. The solubility products of Ti4C2S2 and TiS in austenite are given by

\[
\log [\text{Ti}] [\text{C}] = -15,600/T + 6.50
\]

and

\[
\log [\text{Ti}] [\text{S}] = -17,640/T + 8.20
\]

These lie between the values for TiN and TiC in the austenite temperature range. The solubility products of the precipitates which are often observed in Ti-bearing steels thus increase in the order: TiN < Ti4C2S2 < TiS < MnS < TiC.

3. The volume fraction of stringer inclusions \( (V_s) \) is a function of the weight percent of sulfur \( ([S]) \) and the sulfur partition coefficient \( (P_c) \) and is of the form

\[
V_s = 0.053[S] (1 + 3.34 P_c)^{-0.45}
\]

4. For purposes of sulfide shape control, the optimum level of Ti addition in the presence of 1.5 pct Mn is around five to six times that required to tie up the N present in the form of TiN.

APPENDIX

Normalization of microanalysis data pertaining to mixed Ti sulfide and Mn sulfide inclusions

In this derivation, only the elements Fe, Mn, S, and Ti, which were detectable by the microprobe used in the present work, are taken into account. Since some of the remaining elements, e.g., C and N, are not included, the atom fraction of a given element \( i \) \( (i = \text{Fe, Mn, S, or Ti}) \) must be considered as a relative rather than as an absolute concentration.

We first assume that there are \( N \) atoms present in the volume being analyzed; \( N_M \) of these belong to the matrix and \( N_P \) to the particle. We now define

\[
\alpha = N_M/N \quad \text{and} \quad \beta = N_P/N
\]

so that

\[
\alpha + \beta = 1
\]

The following mass balances are then evident:

\[
X_{\text{Fe}}^R = \alpha X_{\text{Fe}}^M + \beta X_{\text{Fe}}^P
\]

\[
X_{\text{Mn}}^R = \alpha X_{\text{Mn}}^M + \beta X_{\text{Mn}}^P
\]

\[
X_S^R = \alpha X_S^M + \beta X_S^P
\]

\[
X_{\text{Ti}}^R = \alpha X_{\text{Ti}}^M + \beta X_{\text{Ti}}^P
\]

Here, \( X_i^R \) is the atom fraction of element \( i \) as measured in the volume containing the inclusion (i.e., the raw data),
$X_i^M$ is the measured atom fraction of $i$ in the matrix, and $X_i^P$ is the atom fraction of $i$ in the particle. It was found experimentally that

$$X_i^M = 0 \quad [A7]$$

We can further reasonably assume that the sulfide inclusions do not contain any iron, i.e., that

$$X_{Fe}^P = 0 \quad [A8]$$

Substitution of Eqs. [A7] and [A8] into the mass balances given above leads to Eqs. [1] through [5].

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