Effect of Phosphorus on Sulfide Precipitation in Strip Casting Low Carbon Steel

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The effect of phosphorus addition on sulfide precipitation for strip casting low carbon steel containing copper was investigated and discussed with respect to the morphology, size, and composition of sulfide. Both experimental results and mathematical calculation showed that the addition of phosphorus retards the sulfide precipitation at high temperature, promotes the supersaturation of sulfur, and produces more copper bearings and smaller sulfides at low temperature. Phosphorus also promotes sulfide precipitation in γ-Fe instead of in α-Fe, so that small spherical copper sulfides form at a high cooling rate instead of plate-like shaped copper sulfides.

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1. Introduction

Impurities such as phosphorus, sulfur, and copper in steels are generally undesirable in large quantities in steel-making process, since they lead to low toughness, poor weldability, or hot shortness. However, the removal of these impurities from steel results in a large quantity of slag and CO$_2$ exhaust causing much environmental load.

Sulfides in steel also have problems due to their size and morphology. Large sulfides usually result in bad mechanical properties, and non-spherical sulfides cause some properties with anisotropy.

Recently small copper sulfides in strip casting steel were found to increase the mechanical properties considerably. At the same time, a lot of papers discussed the effect of phosphorus on phase transformation and the refining of the as-cast structure. Since the solubility of sulfide and the diffusion behavior of S, Mn, and Cu are quite different according to the iron phases, sulfide precipitation behavior is affected significantly by the type of matrix and temperature. Phosphorus should have some effects on sulfide precipitation based on this factor. However, it has not been clarified yet.

In the present paper, the morphology, size distribution, and composition of sulfide that precipitated in strip casting low carbon steels with and without phosphorus were investigated by Transmission Electron Microscopy (TEM). The effects of phosphorus on sulfides precipitation are discussed with respect to the change of phase transformation by the addition of phosphorus.

2. Experimental Procedures

2.1 Materials and casting conditions

Table 1 shows the chemical composition of the steels (hereafter called low P steel and high P steel respectively) produced by the twin drum caster at the Mitsubishi Heavy Industries Ltd., Hiroshima R&D Center. The contents of the impurities were designed to be slightly higher than those in a normal low carbon steel to simulate the steel scraps. The casting speed was 0.333 m/s, the casting temperature was 1843 ± 20 K, the casting weight was 15 kg, and the mold width was 150 mm. The drum supporting force controlled the thickness of the cast strip to be about 2.0 mm. The strip was radiantly cooled on the transportation rollers table.

2.2 Analysis methods

The precipitates in the strips were observed by TEM. The thin sliced specimens for TEM observation were cut from a bulk with a thickness of 0.2 mm and mechanically ground to 80 μm. φ3 mm foil samples were prepared by electro-polishing at 50 V in an electrochemical solution containing 5 vol% perchloric acid and 95 vol% methanol. Carbon extraction replicas were also prepared through the standard procedures. The replicas were floated on molybdenum grids, and a beryllium specimen holder was used to avoid the possible detection of Cu from the grid and the specimen holder. The TEM observation was performed with a JEM-2000FXII microscope operated at 200 kV and coupled to an energy dispersion spectrometer (EDS).

3. Experimental Results and Discussion

3.1 Morphology, composition and size distribution of sulfides

Sulfides with two kinds of morphology were found in low P steel, spherical and plate-like, as shown in Figs. 1 and 2. The size of spherical sulfides varies considerably, from approximately 1·10$^{-7}$ m to 1.6·10$^{-6}$ m. The large spherical sulfides consist mainly of Mn and S, with some Cu and Fe. When the size of the particles decreased, the content of Cu in sulfides increased as shown in Fig. 1.

The plate-like sulfides consist mainly of Cu and S, with small amounts of Fe and Mn, as shown in Fig. 2. The short
and long axes of the plate-like sulfide are between 5–10 · 10⁻⁸ m and 3–14 · 10⁻⁷ m, respectively. Fig. 2(c) is the diffraction pattern of the plate-like copper sulfide and it shows that the sulfide has a face centered cubic (f.c.c.) structure. About 8% (in number) of the sulfides have a plate-like morphology in low P steel. On the other hand, few plate-like sulfides have been observed in high P steel.

Several detailed investigations have been reported on the plate-like MnS in steel up to now. Matsubara⁶) mentioned that plate-like MnS precipitated on {100} plane in austenite and was semi-coherent with austenite. Recently, Furuhara⁷) confirmed the semi-coherent relationship by High Resolution TEM observation in austenite stainless steel. Kimura⁸) and Yamamoto⁹) observed the precipitation and growth of plate-like MnS in austenite over a certain temperature range by the Confocal Scanning Laser Microscope. Since Cu₂₋₅S and MnS have the similar f.c.c. structure, and the values of the structural parameters are also very close to each other (5.564 · 10⁻¹⁰ m for Cu₂₋₅S and 5.224 · 10⁻¹⁰ m for MnS), it is reasonable to speculate that the present plate-like Cu₂₋₅S precipitated from austenite.

Two distinct characteristics were observed in high P steel compared to low P steel. First is the presence of spherical sulfides as shown in Fig. 3. Most of these spherical sulfides were mainly Cu₂₋₅S (Figs. 3(b) and (d)), and their size was less than 1.5 · 10⁻⁷ m, far less than the size of the sulfides in low P steel. The second is the observation of few plate-like sulfides in high P steel.

The size distribution of spherical sulfides in low and high P steels was analyzed from 30 photos taken at a magnification of 20000. The particles were divided into several size ranges of under 5 · 10⁻⁸ m, (5–10) · 10⁻⁸ m, (1–1.5) · 10⁻⁷ m, and so on. The analyzed size distribution is shown in Fig. 4. The spherical sulfides in low P steel has a wide size distribution, which is from less than 1 · 10⁻⁷ m to more than 1.6 · 10⁻⁶ m. On the other hand, the size distribution in high P steel is from less than 1 · 10⁻⁷ m to about 5 · 10⁻⁷ m. Most of the sulfides in high P steel are smaller than 1.5 · 10⁻⁷ m.

The above experimental results were summarized in Table 2. These experimental results show the effects on sulfides by adding phosphorus in strip steels as follows:
sulfide solubility in $\delta$-Fe and $\gamma$-Fe. Therefore, $\delta/\gamma$ and $\gamma/\alpha$ transformations will cause a lot of MnS precipitation. In addition, Fig. 5(a) also shows that Cu$_2$S has a solubility curve with a steep slope, indicating that Cu$_2$S may have a stronger precipitation tendency than MnS at a low temperature.

Figure 5(b) shows the effects of composition on sulfide precipitation temperature. The precipitation temperature of MnS changes to some degree with Mn and S contents, while for Cu$_2$S it changes slightly from about 1450 to 1550 K when Cu and S contents increase considerably as shown in Fig. 5(b). It means that the solute elements segregation/redistribution during liquid/solid and $\delta/\gamma$ transformation may have great effects on the MnS precipitation but not much effect on the Cu$_2$S precipitation.

Phosphorus is a well known ferrite stabilizing element. Figure 6 shows the effect of phosphorus on the Fe-C phase diagram that was calculated by the thermodynamic calculation software–Thermo-Calc (Sweden). Phosphorus decreases the liquidus and solidus of steel and also has a great effect on $A_{e4}$ and $A_{e3}$ temperature. The addition of 0.1 mass% P in steel may lower $A_{e4}$ by 55 K and raise $A_{e3}$ by 70 K. Since phosphorus segregates very easily during solidification, it may have a greater effect on the local transformation temperature compared to that at the equilibrium phase state. These changes by adding phosphorus should have some effects on element distribution, diffusion and sulfide precip-

### Table 2 Characterization of sulfide precipitates in low and high P steels.

<table>
<thead>
<tr>
<th>Morphology</th>
<th>Size, $\times 10^{-5}$ m</th>
<th>Composition</th>
<th>Number ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Low P steel</strong></td>
<td></td>
<td>(Mn,Cu,Fe)S;Cu$_2$S</td>
<td>92%</td>
</tr>
<tr>
<td>spherical</td>
<td>&lt;1600</td>
<td>Cu$_2$S</td>
<td>8%</td>
</tr>
<tr>
<td>plate-like</td>
<td>(50 × 300)- (100 × 1400)</td>
<td>(Mn,Cu,Fe)S;Cu$_2$S</td>
<td>99.9%</td>
</tr>
<tr>
<td><strong>High P steel</strong></td>
<td></td>
<td>Cu$_2$S</td>
<td>few</td>
</tr>
<tr>
<td>spherical</td>
<td>&lt;600; most &lt;150</td>
<td>Cu$_2$S</td>
<td></td>
</tr>
<tr>
<td>plate-like</td>
<td></td>
<td>Cu$_2$S</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 5 (a) Solubility of MnS and Cu$_2$S in different Fe phases. (b) Effect of composition on MnS and Cu$_2$S precipitation temperature.
itation, since sulfide precipitation is sensitive to the steel composition, diffusion, and temperature.

3.3 Mathematical calculation

Clyne and Kurz’s\(^\text{13}\) mode was often used to calculate the microsegregation of solute elements during solidification. However, only the solid and liquid concentration at the solid/liquid interface during solidification can be obtained and the solidified part concentration during solidification cannot be obtained by that model. In this paper, a modified mathematical model was used to calculate the element redistribution during solidification and \(\delta/\gamma\) transformation as well as sulfide precipitation. Half of the area of the secondary dendrite spacing is set as the calculation domain and is divided into \(N\) \((N = 30)\) nodes as shown in Fig. 7. The calculation is carried out by the direct finite difference method which is described in detail in a previous paper.\(^{14}\) Assuming that the solid fraction is \(f_s\) at the solid/liquid interface at time \(t\), the solid and liquid concentration are \(C_s^t\) and \(C_l^t\), respectively, and from time \(t\) to \(t + dt\), node \(m + 1\) was assumed to be solidified. Then, for one solute element, we have the following mass balance.

\[
(C_s^t - C_s^{t+dt}) \cdot df_s = (1 - f_s - df_s) \cdot (C_s^{t+dt} - C_s^t) + 2akf_s \cdot (C_s^{t+dt} - C_s^t)
\]

where \(\alpha = 4D_s t_s/L^2\), \(D_s\) is the diffusion coefficient in the solid phase, \(k\) is the partition coefficient of the solute element between liquid and solid, \(t_s = (T_L - T_S)/R_c\) is the local solidification time, \(L\) is the second dendrite arm spacing and is set as \(15 \times 10^{-6}\) m in present calculation based on experimental data, \(R_c\) is the cooling rate, and \(T_L\) and \(T_S\) are the liquidus and solidus temperature, respectively.

Then we have

\[
\frac{C_s^t - C_s^{t+dt} - C_s^{t+dt} - C_s^t}{df_s} \cdot (1 - f_s - df_s) \cdot (C_s^{t+dt} - C_s^t) + 2akf_s \cdot (C_s^{t+dt} - C_s^t)
\]

Fig. 7 Schematic showing the solute redistribution with complete liquid mixing and some solid-state diffusion.
From node 1 to node \( m \) at time \( t + dt \), the solid node concentration is calculated as follows.

For the node \( i = 1 \):
\[
C^{i+dt} = C^i \cdot \frac{1 - (f_s + df_s) + df_s + 2\alpha_k f_s}{1 - (f_s + df_s) + kdf_s + 2\alpha_k f_s}
\]
\[
C^i = kC^{i+dt}
\]

The calculated composition is based on 0.088\%C − 0.25\%Si − 0.56\%Mn − 0.017\%S − 0.12\%Cu. Phosphorus is set as 0.013\%P for low P steel and 0.081\%P for high P steel. For such composition, the steels are solidified completely as a δ phase and proceed to a solid δ/γ transformation. The δ/γ transformation starts when the entire domain temperature is just below the \( T_\ell \) that was calculated based on the last node (\( i = 30 \)) composition. The solute redistribution during the δ/γ transformation was calculated by Ueshima’s model.\(^{10}\) The parameters for calculation are listed in Table 3.

### Table 3 Parameters for mathematical calculation\(^{10,12,14,16}\)

<table>
<thead>
<tr>
<th>Elements</th>
<th>( k^{1/1}_{\ell} )</th>
<th>( k^{1/1}_s )</th>
<th>( D^{1/1} ), ( \times 10^{-4} \cdot \text{m}^2/\text{s} )</th>
<th>( D^{1/1} ), ( \times 10^{-4} \cdot \text{m}^2/\text{s} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>0.19</td>
<td>1.79</td>
<td>0.0127 ( \times \exp(−19450/RT) )</td>
<td>0.0761 ( \times \exp(−32160) )</td>
</tr>
<tr>
<td>Si</td>
<td>0.77</td>
<td>0.68</td>
<td>8.0 ( \times \exp(−59500/RT) )</td>
<td>0.30 ( \times \exp(−60100/RT) )</td>
</tr>
<tr>
<td>Mn</td>
<td>0.76</td>
<td>1.03</td>
<td>0.76 ( \times \exp(−53640/RT) )</td>
<td>0.055 ( \times \exp(−59600/RT) )</td>
</tr>
<tr>
<td>P</td>
<td>0.23</td>
<td>0.57</td>
<td>2.9 ( \times \exp(−55000/RT) )</td>
<td>0.010 ( \times \exp(−43700/RT) )</td>
</tr>
<tr>
<td>S</td>
<td>0.05</td>
<td>0.70</td>
<td>4.56 ( \times \exp(−51300/RT) )</td>
<td>2.4 ( \times \exp(−53400/RT) )</td>
</tr>
<tr>
<td>Cu</td>
<td>0.90</td>
<td>0.78</td>
<td>25 ( \times \exp(−62000/RT) )</td>
<td>0.19 ( \times \exp(−65080/RT) )</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Estimated cooling rate, ( R_c ), K/s</th>
<th>On solidification</th>
<th>End of δ/γ transformation</th>
<th>( \log[%\text{Mn}]/%\text{S} = −86727/\ell + 4.745 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>687 K/s ( (L = 688(60R_c)^{-0.38}) )</td>
<td>600 K/s</td>
<td>100 K/s</td>
<td>Solubility of MnS in liquid Fe</td>
</tr>
</tbody>
</table>

3.3.1 Effect of phosphorus on sulfide precipitation during solidification

Figure 8 shows the temperature evolution for low and high P steels during solidification. The liquidus and solidus temperature for the high P steel are lower than those for the low P steel, and this tendency is remarkable especially at the solidus temperature.

During solidification, Mn and S continue to become richer due to the redistribution in the liquid phase; however, for the present calculation composition, the actual product of Mn and S is still much lower than the equilibrium solubility product for both low P and high P steels. Therefore, MnS could not be formed in the liquid phase in either steel.

However, in the solid phase and at the solidus temperature, the actual product of Mn and S is much higher than the equilibrium solubility product in the last solidified zones which is the interdendrite area. A lot of nodes have a higher product of Mn and S than the equilibrium product in high P.
3.3.2 Effect of phosphorus on sulfide precipitation

Effects on small sulfide precipitation at low temperature. Thus, the retarding effect of P on sulfide tendency to allure sulfide precipitating from the matrix at low temperature, the higher the precipitation temperature, the quicker the growth rate for sulfides, and the transformation. In addition, the higher the precipitation also the precipitation amount of MnS during liquid/solid transformation decreases not only the precipitation temperature of MnS but respectively for low and high P steel. Therefore, high P steel, which decreases the segregation degree of S in steel, but the product value is not very high. On the other hand, fewer nodes have a higher product of Mn and S than the equilibrium product in low P steel, but the product value is very high compared to those in high P steel. As shown in Fig. 8, high P steel has a wider temperature range from liquidus temperature to solidus temperature than that of low P steel. Since S is an element with a high diffusion coefficient, there is more time for S to conduct back solid diffusion in high P steel, which decreases the segregation degree of S in the last solidified zones as shown in Fig. 9. Since the solidus temperature is quite different, it may be reasonable if we assume that the undercooling for MnS precipitation is 50 K and 70 K for low and high P steel respectively. Then the S that precipitated as MnS is 0.00413% and 0.00243%, respectively for low and high P steels. Therefore, high P decreases not only the precipitation temperature of MnS but also the precipitation amount of MnS during liquid/solid transformation. In addition, the higher the precipitation temperature, the quicker the growth rate for sulfides, and the more sulfide precipitating at high temperature, the higher the tendency to allure sulfide precipitating from the matrix at low temperature. Thus, the retarding effect of P on sulfide precipitation during solidification may have some active effects on small sulfide precipitation at low temperature.

3.3.3 Effect of phosphorus on sulfide precipitation during $\delta/\gamma$ transformation

The calculated temperature for starting and finishing the $\delta/\gamma$ transformation for low and high P steels is shown in Fig. 10. In high P steel, both the starting and finishing temperature of the $\delta/\gamma$ transformation are considerably decreased compared with those of low P steel. During the $\delta/\gamma$ transformation, S tends to become richer in the $\delta$ phase while Mn tends to become richer in the $\gamma$ phase. Although the Mn and S product is higher than the equilibrium solubility product for all the nodes at the transformation temperature, the sulfide precipitation is usually observed only in the last zone during the $\delta/\gamma$ transformation even for slow cooling rate case. By considering only the MnS precipitation in the last $\delta/\gamma$ transformation node, S that precipitated as MnS is 0.00048% at 1688 K and 0.00053% at 1616 K for low and high P steels, respectively. Although the amount of precipitation is similar, the precipitation temperature in the high P steel is much lower than that in the low P steel. Such kind of low precipitation temperature is helpful for suppressing the sulfide growth.

3.3.3 Effect of phosphorus on sulfide precipitation in $\gamma$-Fe and during $\gamma/\alpha$ transformation

As discussed above, fewer sulfides precipitate at high temperature in the high P steel. It may lead to an increment of the supersaturation degree during sulfide precipitation from the $\gamma$-Fe matrix at low temperature, especially for a high cooling rate case. High supersaturation should result in a high nucleation rate that yields small size particles and may be one of the explanations for the smaller sulfides in high P steel.

The precipitation of Cu$_2$S also becomes possible in austenite for the present calculation steel. Since Cu$_2$S has a sharper solubility curve than that of MnS, the supersaturation degree for Cu$_2$S is expected to be larger than that for MnS. Therefore, the necessary undercooling for the precipitation of Cu$_2$S may be lower than that of MnS. By considering the same activation energy for nucleation, the necessary undercooling for Cu$_2$S is assumed as half of that for MnS in present calculation. Figures 11(a) and (c) show the precipitation of sulfides for the two steels by assuming that the undercooling for precipitation from $\gamma$-Fe is 500 K and 250 K for MnS and Cu$_2$S, respectively. Figures 11(b) and 11(d) show the sulfide precipitation for the case that the MnS precipitation from $\gamma$-Fe was completely suppressed (undercooling for MnS is 600 K), which is possible at high cooling rates.

According to Fig. 11, most of Cu$_2$S precipitated from $\gamma$-Fe in low P steel. However, in high P steel only some of Cu$_2$S
precipitated from $\gamma$-Fe and most of Cu$_2$S precipitated from $\alpha$-Fe when the cooling rate is high. It means that a high cooling rate promotes S to precipitate as Cu$_2$S instead of as MnS; while high P promotes S to precipitate from $\gamma$-Fe-Fe instead of from $\alpha$-Fe.

Since plate-like Cu$_2$S is semi-coherent with $\gamma$-Fe and precipitates from $\gamma$-Fe, it is clear why some plate-like Cu$_2$S could be observed in low P steel while few could be observed in high P steel.

Assuming that the critical undercooling ($\Delta T$) for MnS precipitation from $\gamma$-Fe has the following relationship with the cooling rate ($R_c$),

$$\Delta T = a(R_c)^{1/4}$$

According to the experiment data$^8$ for the 0.04%C-0.21%Mn-0.012%S steel, the starting temperature for MnS precipitation from $\gamma$-Fe is about 1500 K. Therefore, $a$ could be determined to be about 170. Then we could estimate the relationship between S precipitated as MnS or Cu$_2$S and the cooling rate as shown in Fig. 12. At a low cooling rate, most of the S precipitated as MnS at a high temperature, while only a few S could be precipitated as Cu$_2$S at a low temperature. By increasing the cooling rate, MnS precipitating at a high temperature is suppressed, and the S that precipitated as Cu$_2$S at a low temperature increases. The amount of MnS precipitation during solidification was decreased due to the P addition, and the S that precipitated as Cu$_2$S at a low temperature increased in high P steel. In addition, phosphorus decreases the MnS precipitation temperature during solidification and $\delta/\gamma$ transformation to a lower stage. It helps the high cooling rate to suppress MnS precipitation since high cooling rate has more suppressing effect if the precipitation occurs at a low temperature with the same supersaturation.

Fig. 11 Precipitation of MnS and Cu$_2$S in different stages (a) 500 K undercooling for MnS, low P steel, (b) 600 K undercooling for MnS, low P steel, (c) 500 K undercooling for MnS, high P steel, (d) 600 K undercooling for MnS, high P steel.

Fig. 12 Estimated effect of cooling rate on MnS and Cu$_2$S precipitation.
4. Conclusion

The morphology, size distribution and composition of sulfides which precipitated in strip casting low carbon steel with and without phosphorus were investigated by TEM. The following results were obtained:

1) Both spherical and plate-like sulfides exist in low phosphorus steel. Spherical sulfides are mainly MnS, and the content of Cu$_2$S increases with a decrease in particle size. Plate-like sulfides are Cu$_2$S which are considered to precipitate from γ-Fe.

2) Very few plate-like sulfides are observed in high phosphorus steel. Spherical sulfides are mainly Cu$_2$S, and their sizes are smaller than those in low phosphorus steel.

3) Mathematical calculation shows that phosphorus lowers the MnS precipitation temperature and decreases the amount of precipitation during solidification. Phosphorus also lowers the MnS precipitation temperature significantly during the δ/γ transformation. All of these factors result from the effects of phosphorus on the phase transformation temperature.

4) Manganese sulfide has advantages in precipitation at high temperature, while Cu$_2$S does at low temperature. A high cooling rate can suppress MnS precipitation at high temperature and then promotes Cu$_2$S precipitation at low temperature. Phosphorus promotes Cu$_2$S precipitation in α-Fe instead of in γ-Fe and changes the morphology of Cu$_2$S from plate-like to spherical.

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REFERENCES