**In-situ** Observation of the $\delta/\gamma$ Phase Transformation on the Surface of Low Carbon Steel Containing Phosphorus at Various Cooling Rates

Zhongzhu LIU,1) Yoshinao KOBAYASHI,2) Jian YANG,1) Kotobu NAGAI2) and Mamoru KUWABARA1)

1) Graduate School of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8603 Japan.
2) Steel Research Center, National Institute for Materials Science, 1-2-1 Sengen, Tsukuba 305-0047 Japan.

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In this paper, the solid $\delta/\gamma$ phase transformation is observed "in-situ" on the surface of low carbon steels containing different phosphorus concentrations by the Confocal Scanning Laser Microscope (CSLM) at various cooling rates. The effects of phosphorus and cooling rate on the $\delta/\gamma$ phase transformation are discussed based on the experimental results and mathematical calculation. Phosphorus is shown to decrease the $T_{A4}$ temperature and to increase the $T_{A3}$ temperature at various cooling rates. This effect is enhanced by the redistribution of phosphorus from the $\gamma$ phase to the $\delta$ phase during the transformation. Some retained $\delta$ phase is kept until the $\gamma/\alpha$ phase transformation in steel containing high phosphorus (0.2% P). The retained $\delta$ phase could retard the $\gamma$ grain growth and promote the $\alpha$ phase precipitation. At the slow cooling rate, the $\gamma$ cells appear first from the triple points or $\delta$ grain boundaries and then spread with finger-like patterns. While at the rapid cooling rate, the $\gamma$ cells appear first from the $\delta$ grain boundaries with sword-like patterns, and spread sharply into both sides of initial $\delta$ grain boundary.

KEY WORDS: in-situ observation; phase transformation; phosphorus; low carbon steel; cooling rate; grain boundary.

1. Introduction

Some novel processes, such as thin slab continuous casting and compact rolling process/thermo-mechanical treatment,1,2) have recently become popular throughout the world, and some other novel processes such as cross-rolling are now been studied.3) Such novel processes have encouraged people to reconsider some elements’ roles in steel with more comprehensive views. For example, the harmful effects in the conventional continuous casting and rolling process that are caused by some impurities could be reduced, and these impurities may become beneficial elements in such novel processes. Phosphorus, which is usually considered to be an impurity in steel, has been reported to have great effects on phase transformation and to refine the prior-austenite grain size during the solidification process.4–6) Phosphorus also causes some effects on sulfide precipitation in steel,7) such as promoting the sulfide to precipitate at a smaller size.

Unfortunately, most of the above results were based on the observation of samples that were taken at ambient temperature as well as on some mathematical calculations. Until now, there seemed to be no direct experimental data, such as an "in-situ" observation of the phase transformation and grain growth in the steel containing high phosphorus at high temperatures. However, the Confocal Scanning Laser Microscope (CSLM) has recently provided the convenient possibility of making an “in-situ” observation of the phase transformation on the surface of samples at high temperature. Reid8) recently reviewed the development history of CSLM and made a detailed description of the advantages and limitations of CSLM by comparing it with other established techniques to study the microstructural development at high temperatures, such as X-ray transmission experimental techniques, directional solidification studies, optical and electron microscopy, high temperature transmission electron microscopy and thermionic transmission microscopy. A more enhanced understanding of the solid state phase transformation is being anticipated by the CSLM.

Since the 1990’s, Yin,9,10) Kimura,11) Hasegawa12) and Phelan13,14) have used the CSLM to make an “in-situ” observation of the phase transformation or sulfide precipitation on the surface of steels at low cooling rates (usually about 0.33 K/s). However, there are still no direct data on the effects of the steel composition, such as phosphorus, and different cooling rates on the phase transformation. In this paper, the $\delta \rightarrow \gamma$ phase transformation is observed on the surface of low carbon steels with different phosphorus concentration by the CSLM at various cooling rates. The effects of phosphorus and cooling rates on the $\delta \rightarrow \gamma$ transformation are discussed based on the experimental results and mathematical calculation.
2. Experimental Procedures

Three kinds of as-cast low carbon steel: Low Phosphorus Steel (LPS), Medium Phosphorus Steel (MPS) and High Phosphorus Steel (HPS) were used in this experiment. The chemical compositions of these steels are shown in Table 1. The LPS and MPS samples were cast by the twin drum caster at the Mitsubishi Heavy Industries Ltd., Hiroshima R&D Center. The thickness of the cast strips was about 2.2 mm. A more detailed description of that casting process was mentioned in a previous paper. The HPS sample was produced in the laboratory. About 3 kg of pure electrolytic iron was melted in a vacuum induction furnace, then alloyed and cast into a water cooled copper mould with a 3 mm thickness. All the samples were machined into a disc (5.0 mm in diameter and 2 mm in height) and the surface was mirror polished before the “in-situ” observation.

A CSLM with an infrared image furnace was employed for the “in-situ” observation. The details of the principle and the method of operation are the same as those that are described by Yin, Kimura and Hasegawa. The sample was heated and cooled in an alumina crucible (5.3 mm in inner diameter) under an ultra-high purity argon gas. The temperature was measured at the bottom of the holder of the crucible. According to Shibata’s reports, when the sample was heated to 1050 K at a rate of 1.67 K/s, the actual temperature on the surface of the sample (4.3 mm in diameter and 2 mm in height) was almost the same as the temperature that was measured at the bottom of the holder. A difference between these two temperatures gradually appeared when the temperature increased to more than 1100 K. When the temperature was 1670 K at the bottom of the holder, the temperatures at the center and the edge of the sample surface were about 1650 K and 1630 K, respectively. In this experiment, the observation point was fixed at the similar site on the surface of all the samples, and the difference in temperature between the surface and the bottom of the sample was treated as a systematic error and was not taken into consideration.

Two kinds of cooling rates were conducted in this experiment to investigate the effects of the cooling rates on the phase transformation in steel, as shown in Fig. 1(a). The heating rate was fixed at 1.67 K/s, and the cooling rates were set as 0.33 K/s for the slow cooling rate and 10 K/s for rapid cooling rate after holding the samples at 1723 K for 1200 s. Unfortunately, the actual cooling rate did not follow the designated one for the rapid cooling rate when the temperature was below 700 K, as shown in Fig. 1(b). However, the results were not affected if only the phase transformation that occurred at temperatures above 700 K were considered.

3. Experimental Results

3.1. δ→γ Phase Transformation at the Slow Cooling Rate

The solid δ→γ transformation sequences at the slow cooling rate for LPS and MPS are shown in Figs. 2 and 3, respectively. The δ-ferrites usually have a hexagon shape after merging and coarsening at high temperature, as shown in Fig. 3(a). The start of the δ→γ transformation (the ap-

<table>
<thead>
<tr>
<th>Sample</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
<th>Sol. Al</th>
<th>S</th>
<th>Cu</th>
<th>O</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>LPS</td>
<td>0.096</td>
<td>0.26</td>
<td>0.61</td>
<td>0.013</td>
<td>0.065</td>
<td>0.016</td>
<td>0.12</td>
<td>0.004</td>
<td>0.020</td>
</tr>
<tr>
<td>MPS</td>
<td>0.088</td>
<td>0.25</td>
<td>0.56</td>
<td>0.081</td>
<td>0.095</td>
<td>0.017</td>
<td>0.12</td>
<td>0.004</td>
<td>0.027</td>
</tr>
<tr>
<td>HPS</td>
<td>0.074</td>
<td>0.15</td>
<td>0.68</td>
<td>0.19</td>
<td>0.002</td>
<td>0.059</td>
<td>0.89</td>
<td>&lt;0.005</td>
<td>&lt;0.005</td>
</tr>
</tbody>
</table>

Fig. 1. The temperature histories of samples. (a) The history of the set values for the slow and rapid cooling rates; (b) the actual temperature history for the rapid cooling rate.

Fig. 2. Solid δ/γ transformation sequence in the LPS sample, slow cooling rate (GB means grain boundary). (a) Just before the start of the transformation; (f) end of the transformation.
searchers made detailed “in-situ” observations of the transformation at some holding temperature or at a low cooling rate. The above process during continuous cooling agrees with the description by Yin et al. 9,10, Phelan, et al., 13,14 where both researchers made detailed “in-situ” observations of the \(\delta\rightarrow\gamma\) transformation at some holding temperature or at a low cooling rate.

The observed starting temperatures of the \(\delta\rightarrow\gamma\) transformation \(T_s\), at which the \(\gamma\)-cells first appear) in the LPS and MPS samples are very close at about 1 698–1 701 K. However, as the transformation continues, the transformation process in the MPS becomes slower than that in the LPS, and the finishing temperature of the \(\delta\rightarrow\gamma\) transformation is much lower than that of the LPS at about 1 653 K. The total times for the \(\delta\rightarrow\gamma\) transformation of the LPS and MPS samples are about 142 s and 356 s, respectively. The transformation process in the MPS was greatly retarded compared to that in the LPS, especially in the last quarter stage of the transformation process because of the addition of phosphorus.

Figures 2(e)–2(f) and 3(e)–3(f) show that despite the difference in the transformation temperature sulfides only precipitate from the \(\delta\)-ferrite in the final stage of the \(\delta\rightarrow\gamma\) transformation in the LPS and MPS samples.

After the \(\gamma\)-cells spread and cover the whole \(\delta\)-ferrite grain, the new \(\gamma\)-austenite grain boundaries begin to appear very quickly, as shown in Fig. 3(f). Although the size of the \(\gamma\)-austenite grain at the end of the \(\delta\rightarrow\gamma\) transformation should be about half of the size of the mother \(\delta\)-ferrite as analyzed by Yin et al., 9 the observed size of the new \(\gamma\)-austenite grain on the sample surface is usually larger than the mother \(\delta\)-ferrite grain, which may indicate that the \(\gamma\)-austenite grains coarsen very quickly just after the \(\delta\rightarrow\gamma\) transformation as calculated by Yoshida et al. 4,5.

The HPS sample contained higher phosphorus as well as higher copper and sulfur contents compared to the LPS and MPS samples. During the experiment, the HPS sample was only held for 90 s at 1 723 K since the surface of the sample appeared to be slightly melted at that temperature. The heating and cooling rates of the HPS sample were the same as those of the LPS and MPS samples. The start of the \(\delta\rightarrow\gamma\) phase transformation was observed at about 1 684 K. The \(\gamma\)-cells precipitated first at the triple point of the \(\delta\)-GBs, then gradually spread along the \(\delta\)-GBs, and also developed into the \(\delta\)-ferrite matrix with the “finger-like” patterns, as shown in Fig. 4. This process was similar to those observed in the LPS and MPS samples, except that it was much slower in the HPS sample. The \(\delta\) phase gradually transformed into the \(\gamma\) phase with decreasing temperature. However, unlike the LPS and MPS samples where the initial \(\delta\) phase was completely transformed into the \(\gamma\) phase at the \(T_s\) temperature, the transformation almost stopped without completion at about 1 373 K in the HPS sample. Both the \(\delta\) phase and \(\gamma\) phase appeared to be stable below that temperature.

When the temperature was below 1 373 K, there was no further \(\delta\rightarrow\gamma\) phase transformation (the moving of the \(\delta\)/\(\gamma\) interface) was observed until 1 069 K. At
1069 K, the start of the $\gamma \rightarrow \delta$ transformation (the appearance of the Widmanstatten pattern) was observed from the $\gamma$ grain boundaries and the retained $\delta$ phase.

### 3.2. $\delta \rightarrow \gamma$ Phase Transformation at the Rapid Cooling Rate

The $\delta \rightarrow \gamma$ transformation processes for the LPS and MPS samples at the rapid cooling rate are shown in Figs. 5 and 6, respectively. The start of the $\delta \rightarrow \gamma$ transformation is different from that at the slow cooling rate and is not observed at the triple point of $\delta$-GBs but at the grain boundaries. Sometimes oxide inclusion seems to promote the $\gamma$-cells nucleation, especially when the oxide inclusions are on the grain boundary. The initially nucleated $\gamma$-cells at the rapid cooling rate do not have the trihedral or dihedral shapes as observed at the slow cooling rate, but have a "sword-like" pattern (as shown in Figs. 5(b) and 6(b)) which shows a similarity to the Widmanstatten pattern for the $\gamma \rightarrow \alpha$ transformation. This kind of morphology is rarely observed at the slow cooling rate in the $\delta/\gamma$ transformation process but is often observed in the $\gamma/\alpha$ transformation process. The "sword-like" $\gamma$-cells are inserted first into both sides of the matrix from the $\delta$-GB along the same direction (Fig. 5(b)) or a different direction (Fig. 6(b)). Then these $\gamma$-cells develop quickly along the longitudinal direction and slowly in the lateral direction (Fig. 5(c)). The growth along the longitudinal direction is completed early due to a conflict that occurs with other $\gamma$-cells. The $\gamma$-cells then spread in the lateral direction and gradually cover the whole $\delta$-ferrite grain. The interface morphologies between the $\delta$-ferrite and $\gamma$-cells are initially plane-like during the spreading process; while most of these morphologies change due to very quick curving, and these conditions can be observed particularly in the MPS sample as shown in Fig. 6(c). A finger-like pattern, which is the fully developed curve interface, is not observed as clearly for the rapid cooling rate.

The total time for the $\delta \rightarrow \gamma$ transformation of the LPS and MPS samples is about 8 s and 14 s, respectively, which are considerably shorter than those at the slow cooling rate. Both the starting and finishing transformation temperatures show a higher reduction by the rapid cooling rate compared to those at the slow cooling rate, as shown in Fig. 7. The starting temperature of the MPS is slightly lower than that of the LPS but the finishing temperature of the MPS is much lower than that of the LPS, at both the slow and rapid cooling rates.

The sulfides were also observed precipitating from the $\delta$-ferrite only in the last stage of the $\delta \rightarrow \gamma$ transformation at the rapid cooling rate, which is similar to that observed at the slow cooling rate.

Table 2 summarizes the nucleation sites and the morphology evolution of the $\gamma$-cells during the $\delta \rightarrow \gamma$ transformation process for both the slow and rapid cooling rates.
3.3. \( \gamma \rightarrow \alpha \) Transformation

The \( \gamma \rightarrow \alpha \) transformations in all the samples at both the slow and rapid cooling rates are revealed to be typical Widmanstätten ferrite nucleating and spreading processes as shown in Figs. 8 and 9, where the particles covering the grains are sulfides that precipitated in the \( \gamma \)-Fe phase during cooling. That process agrees with the description of the Widmanstätten ferrite formation from a \( \gamma \) grain boundary by Hanamura,\(^\text{16)}\) who made an “in-situ” observation of ferrite formation from oxide, MnS and a \( \gamma \) grain boundary.

The starting and finishing temperatures of the \( \gamma \rightarrow \alpha \) transformation are quite different from each other for the MPS and LPS samples. At the slow cooling rate, the starting and finishing temperatures of the LPS sample are about 998 K and 953 K, respectively; while they are about 1009 K and 977 K, respectively for the MPS sample. Both the starting and finishing temperatures of the MPS are higher than those of the LPS sample, which are caused by the increase in the \( T_A3 \) temperature that occurred by the phosphorous addition as analyzed by Yoshida\(^\text{4,5)}\) and Liu.\(^\text{7)}\) This becomes more apparent at the rapid cooling rate as shown in Fig. 10.

4. Discussion

4.1. Mathematical Model

Ueshima’s mathematical model\(^\text{17,18)}\) was used to calculate the redistribution of solutes during the \( \delta / \gamma \) transformation process in this paper. The calculated domain is shown schematically in Fig. 11. One sixth of a hexagon with a side of \( 1.2 \times 10^{-2} \) m, which is typical for a \( \delta \)-ferrite grain that was observed in this experiment at high temperature, was divided into 50 nodes. The \( \delta / \gamma \) transformation starts when the temperature of the entire domain is just below \( T_A4 \), which was calculated from the last node (i=50) composition plus some degree of undercooling temperature based on the “in-situ” observed data. The \( T_A4 \) temperatures were calculated by the following equations.\(^\text{4)}\)

\[
T_A4 = 1665 + 1122[\%C] - 60[\%Si] + 12[\%Mn] - 550[\%P] - 160[\%S], \quad \text{K} \quad \ldots \ldots (1)
\]

The calculation is carried out by the direct finite difference method, which is described in detail in a previous paper.\(^\text{7,19)}\) The parameters for the calculations are listed in Table 3.\(^\text{20–24)}\) The solutes concentrations in the \( \delta \) and \( \gamma \) phases are assumed to be in equilibrium at the \( \delta / \gamma \) interface. If the node \( m \) is a \( \gamma \)-phase and the node \( m-1 \) is a \( \delta \)-phase, for every solute element at time \( t \) and temperature \( T \),
Table 3. Parameters of the solute elements for mathematical calculation.19–22)

<table>
<thead>
<tr>
<th>Elements, i</th>
<th>$k_{i}\cdot d$</th>
<th>$D_{i}^{s}, \times 10^{-5} m^{2}/s$</th>
<th>$D_{i}^{f}, \times 10^{-5} m^{2}/s$</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>1.79</td>
<td>0.0127$\cdot$exp(-19450/RT)</td>
<td>0.0761$\cdot$exp(-32160)</td>
</tr>
<tr>
<td>Si</td>
<td>0.68</td>
<td>8.0$\cdot$exp(-59500/RT)</td>
<td>0.30$\cdot$exp(-60100/RT)</td>
</tr>
<tr>
<td>Mn</td>
<td>1.03</td>
<td>0.76$\cdot$exp(-53640/RT)</td>
<td>0.055$\cdot$exp(-59600/RT)</td>
</tr>
<tr>
<td>P</td>
<td>0.57</td>
<td>2.9$\cdot$exp(-55000/RT)</td>
<td>0.010$\cdot$exp(-43700/RT)</td>
</tr>
<tr>
<td>S</td>
<td>0.70</td>
<td>4.56$\cdot$exp(-51300/RT)</td>
<td>2.4$\cdot$exp(-53400/RT)</td>
</tr>
<tr>
<td>Cu</td>
<td>0.78</td>
<td>25$\cdot$exp(-62000/RT)</td>
<td>0.19$\cdot$exp(-65080/RT)</td>
</tr>
</tbody>
</table>

where $k_{i}\cdot d$ is the partition coefficient of the solute elements between γ-austenite and δ-ferrite.

we have

$$C_{i}^{s}=\frac{k_{i}^{s}C_{i}^{s}}{k_{i}^{s}+k_{i}^{f}},$$

$$C_{i}^{f}=\frac{k_{i}^{f}C_{i}^{f}}{k_{i}^{s}+k_{i}^{f}}$$

From time $t$ to time $t+\Delta t$, if the node $m-1$ does not transform into the γ-phase, we have

$$\frac{dC_{i}^{s}-C_{i}^{s}}{dt}=D_{i}^{s}L_{i}(C_{i}^{s}-C_{i}^{s})-L_{i}(C_{i}^{s}-C_{i}^{s}),$$

for $1<i<m-1$ ($D=D^{s}$) and $m<i<50$ ($D=D^{f}$);

$$\frac{dC_{i}^{s}-C_{i}^{s}}{dt}=D_{i}^{s}L_{i}(C_{i}^{s}-C_{i}^{s})-L_{i}(C_{i}^{s}-C_{i}^{s}),$$

for $i=1$;

$$\frac{dC_{i}^{s}-C_{i}^{s}}{dt}=D_{i}^{s}L_{i}(C_{i}^{s}-C_{i}^{s})-L_{i}(C_{i}^{s}-C_{i}^{s})$$

where $C_{i}^{s}$ is the solute concentration in the node $i$ at time $t$, $A_{i}$ is the area of the node $i$, $L_{i}$ is the length of the interface between the $i$-th and $i+1$st node, $D_{i}^{s}$ and $D_{i}^{f}$ are the diffusion coefficients of the solute elements in the δ-phase and γ-phase, respectively, $dx$ is the width of every node, and $R_{c}$ is the cooling rate.

At time $t$ when the entire domain temperature $T$ is just lower than $T_{Ah}, m-1$, the node $m-1$ transforms from the δ-phase to the γ-phase, where $T_{Ah}, m-1$ is the transformation temperature of the node $m-1$ which is calculated from the solute concentrations in the node $m-1$ at time $t$ according to Eq. (1).

According to the partition coefficients listed in Table 3, phosphorus and sulfur are redistributed from the γ-phase to the δ-phase; while manganese is redistributed slightly from the δ-ferrite to the γ-phase during the δ/γ transformation. Thus, the concentration of phosphorus and sulfur in the δ-phase may become very high in the final stage of the δ/γ transformation.

4.2. Effect of Phosphorus on δ/γ Transformation Temperature

Yoshida4) and Liu7) presented a detailed discussion on the effects of phosphorus on the δ/γ transformation and the γ/α transformation based on the phase diagram and thermodynamic calculation. In brief, phosphorus could greatly reduce the $T_{Ah}$ temperature and increase the $T_{A3}$ temperature under the equilibrium condition. However, some degree of undercooling is always necessary for transformation under the non-equilibrium condition. The calculated $T_{Ah}$ temperature based on Eq. (1) and the observed starting temperature of the δ/γ transformation are listed in Table 4. The difference between them is treated as the undercooling in this paper. Table 4 shows that the undercooling for the δ/γ transformation increases with the cooling rate. In addition, the undercooling for the δ/γ transformation of the MPS sample is much lower than that of the LPS sample, especially at the slow cooling rate, which may indicate that while phosphorus reduces the δ/γ transformation temperature, it also reduces the undercooling degree for that transformation.

If we use the observed data for the starting temperature of the δ/γ transformation in the calculation, the calculated transformation process can be shown as the curves in Fig. 12. Here the end of the transformation is defined at the temperature where the γ-austenite ratio $f_\gamma$ becomes 0.99. As shown in Fig. 12, the observed transformation finishing temperatures seem to agree well with the calculated data.
which may indicate that the above treatment is reasonable.

There is not much difference in the transformation temperature in the early stage of the $\delta \rightarrow \gamma$ transformation in the MPS and LPS samples for both the rapid and slow cooling rates. At that stage the difference in the phosphorus concentration in the MPS and LPS samples is not very large, that is 0.081% - 0.013% = 0.068%. However, at the last stage of the transformation, that difference becomes much larger due to the phosphorus that is gradually re-distributed from the $\gamma$-phase to the $\delta$-phase, for example that difference increases to about 0.14% at the rapid cooling rate, which means that the effect of phosphorus on the transformation is more apparent in the last stage of transformation due to the gradually increased phosphorus concentration in the un-transformed $\delta$-phase.

In the HPS sample, the retained $\delta$ phase was kept until the $\gamma/\alpha$ transformation. According to the Fe–P phase diagram,[25] the $\gamma$-area shrinks as a $\gamma$ loop when the concentration of phosphorus in the Fe–P system exceeds 0.31%. Both the $\gamma$-phase and the $\delta$-phase are stable in the system if the concentration of phosphorus is between 0.31% and 0.69%. If the concentration of phosphorus is above 0.69%, there is no $\delta/\gamma$ transformation during cooling. These retained $\delta$-phases could prohibit the growth of $\gamma$ grains and promote the $\alpha$ phase precipitation which may result in a fine as-cast structure during solidification.

5. Conclusions

The solid $\delta/\gamma$ phase transformation was observed on the surface of low carbon steels with different phosphorus concentrations by the CSLM at various cooling rates. The effects of phosphorus and cooling rates on the phase transformation were discussed based on the experimental results and mathematical calculation. The following results were obtained:

1) At the slow cooling rate, the $\gamma$-cells appear first from the triple points or $\delta$ grain boundaries and then spread with finger-like patterns. While at the rapid cooling rate, the $\gamma$-cells appear first from the $\delta$ grain boundaries with sword-like patterns, and spread sharply into both sides of initial $\delta$ grain boundary.

2) The transformation starts at a lower temperature in the high phosphorus steel, and the transformation process is clearly slower than that in the low phosphorus steel, especially in the last stage of the transformation process. In the steel with 0.2% phosphorus, some $\delta$ phases are retained and do not transform into the $\gamma$ phase.

3) There is not much difference in the starting transformation temperature for the low and high phosphorus steels; however, that difference becomes apparent in the finishing transformation temperature.

4) Phosphorus reduces the $T_{\alpha A}$ temperature and increases the $T_{\gamma A}$ temperature at various cooling rates. These effects could be increased by the phosphorus re-distribution during transformation.

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