Influence of Phosphorus on Solidification Structure in Continuously Cast 0.1 mass% Carbon Steel

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In 0.1 mass% carbon steels with phosphorus contents ranging from 0.01 to 0.2 mass%, slabs were continuously cast to a thickness of 100 mm with a laboratory scale caster. Their macro- and micro-structures were characterized, focusing on the effects of phosphorus addition on the structural evolution during solidification and subsequent cooling. Cast slabs of high phosphorus steels have a fine columnar-γ-grain structure. The mean width of the columnar grain was approximately half of that in the cast slabs without the phosphorus addition. Dispersed globular α grains were observed in the α grain structure of high phosphorus steels. The globular grains evolved at the phosphorus-rich spots in the prior-γ grain. The micro-segregation of phosphorus results in these structural evolutions. Since the phosphorus enrichment stabilizes bcc (δ or α) phase locally at the inter-dendritic region, the phosphorus-rich spot makes δ phase retained to lower temperature for the δ/γ transformation, and provides a predominant site for the γ/α transformation. In the high phosphorus casts, therefore, the dispersed δ phase are thought to pin the γ grain growth more effectively in the δ+γ region when the completion of the δ/γ transformation is remarkably suppressed by the phosphorus segregation.

KEY WORDS: low carbon steel; continuous casting; solidification; phosphorous; segregation; phase transformation; austenite; delta ferrite.

1. Introduction

Over the past decade, the thin slab continuous casting and compact rolling process has become popular1,2) since the process has been economically acceptable for the mass production of sheets, especially for low grade steels from scraps. The control of grain structure is essential in the process, since the structure affects hot ductility as well as final mechanical properties. Coarsening of γ grains is one of the serious problems in the continuous casting and the subsequent process, especially in hot direct rolling. It may cause hot surface cracking of slabs in low alloy steels, since the hot ductility depends largely on the γ grain size3–5) and the intergranular fracture in the γ phase results in the surface cracks3–5) Thus it is important to clarify the mechanism of the γ structure evolution after solidification.

Several studies3,10–13) have been made on the evolution of the γ grain structure and on the prevention of its coarsening in carbon steels. The knowledge that have been acquired are mentioned below:

(1) Grain size of γ in the as-cast steels depends on the alloying elements and its content.3,10,13)
(2) Grain size decreases with an increase in the cooling rate.10)
(3) Rapid grain growth of γ occurs immediately after the completion of the transformation into a γ single phase, or below the transformation completion temperature (Tγ).3,10–13)
(4) Pinning of the γ grain boundary is prominent in the existence of the δ phase or the liquid phase in the duplex region above Tγ.3,10–13)
(5) Retardation of grain growth is due to the addition of the bcc-stabilizing element that lowers Tγ.10,13)
(6) Retardation of grain growth is partly due to the dendritic micro-segregation that also lowers Tγ.12–14)

Based on the above conditions, the fine-grained γ structure in low carbon steels can be achieved by optimal alloying, which stabilizes bcc effectively and causes dendritic micro-segregation to some extent. Figure 1 shows a schematic phase diagram in a Fe–M (bcc-stabilizing element) binary system. The Fe binary alloy containing a bcc-stabilizing element has a closed γ single phase region, or the γ-loop, in the Fe-rich side of the phase diagram.15) Such alloying element narrows the γ single phase region by decreasing the Ac (δ/γ) transformation temperature and increasing the Ae3 (γ/α) transformation temperature. Several well-known bcc-stabilizing elements are shown in Table 1. Phosphorus is the strongest bcc-stabilizer. It has such high gradients of transformation temperature per unit content, kAc and kAe, that it most effectively lowers Ac and raises Ae. In addition, phosphorus has a fairly low equilibrium distribution coefficient, kγ, in solidification. Hence, phosphorus addition should be recognized as an extremely effective way to suppress the grain growth of γ in the as-cast
condition. Very few studies have been made on the effect of phosphorus addition on the as-cast structure.

Phosphorus addition brings about solid solution strengthening as well as the bcc-stabilizing in low alloy steels. However, phosphorus is one of the major impurities that are unfavorable in steel making, since high phosphorus causes low toughness and poor weldability. Grain refining by thermo-mechanical treatment improves both strength and toughness in the high phosphorus steels, using the novel process or the cross rolling. Thus, the harmful effects of phosphorus can be suppressed.

Consequently, we have focused on the effect of phosphorus on the micro-structural evolution during solidification and subsequent cooling, especially on the γ grain growth in the present study. Macro- and micro-structures of continuously cast (CC) 100 mm thick slab of 0.1 mass% carbon steels with various phosphorus contents have been characterized and discussed in terms of the effect of phosphorus.

2. Experimental

2.1. Materials

Three kinds of steel were characterized. Their base compositions are 0.1C–0.15Si–0.6Mn in mass% and the phosphorus (P) content ranges between 0.01 and 0.20 mass%, i.e. 0.01P, 0.10P and 0.20P. The chemical compositions of the test steels are listed in Table 2. The equilibrium in the Fe–C–Si–Mn–P system, including the range of the present steels, is calculated by the thermodynamic application, ThermoCalc, and the multi-component system database, SSOL. Figure 2(a) shows the phase diagram of the Fe (0.1C–0.15Si–0.6Mn, in mass%)–P pseudo-binary system. This steel system has a typical γ-loop and a negative high gradient of δ/γ transformation temperature, or $k_{A4}$, due to the bcc-stabilizing effect that is shown in Fig. 1. Figure 2(b)

![Fig. 1. Schematic phase diagram of a Fe–M (bcc-stabilizing element) binary alloy.](image-url)

<table>
<thead>
<tr>
<th>Element</th>
<th>Al</th>
<th>Be</th>
<th>Cr</th>
<th>Mo</th>
<th>P</th>
<th>Si</th>
<th>Ti</th>
<th>V</th>
<th>W</th>
</tr>
</thead>
<tbody>
<tr>
<td>C\text{γ-loop}[mass%]</td>
<td>$^*$1</td>
<td>0.78</td>
<td>0.33</td>
<td>11.5</td>
<td>2.83</td>
<td>0.33</td>
<td>1.73</td>
<td>0.75</td>
<td>1.27</td>
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<tr>
<td>$^*$2</td>
<td>0.63</td>
<td>0.04</td>
<td>11.2</td>
<td>2.85</td>
<td>0.31</td>
<td>1.63</td>
<td>0.69</td>
<td>1.28</td>
<td>4.62</td>
</tr>
<tr>
<td>$k_{A4}$(K/mass%)</td>
<td>$^*$3</td>
<td>-81</td>
<td>-750</td>
<td>-1.5</td>
<td>-46</td>
<td>-550</td>
<td>-52</td>
<td>-140</td>
<td>-80</td>
</tr>
<tr>
<td>$^*$4</td>
<td>-1460</td>
<td>-7</td>
<td>-37</td>
<td>-140</td>
<td>-60</td>
<td>-</td>
<td>-67</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>$k_{A3}$(K/mass%)</td>
<td>$^*$3</td>
<td>+140</td>
<td>+190</td>
<td>-16</td>
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<td>+340</td>
<td>+77</td>
<td>+180</td>
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<td>-</td>
<td>-</td>
<td>+31.5</td>
<td>+700</td>
<td>+44.7</td>
<td>+400</td>
<td>+104</td>
<td>+13.1</td>
</tr>
<tr>
<td>$k^{\text{L}}$(L)</td>
<td>$^*$5</td>
<td>1.0</td>
<td>0.90</td>
<td>0.89</td>
<td>0.81</td>
<td>0.32</td>
<td>0.61</td>
<td>0.28</td>
<td>0.84</td>
</tr>
<tr>
<td>$^*$6</td>
<td>0.6</td>
<td>-</td>
<td>0.89</td>
<td>0.7</td>
<td>0.13</td>
<td>0.6</td>
<td>0.14</td>
<td>0.9</td>
<td>-0.06</td>
</tr>
</tbody>
</table>

*1: The $C_{\text{γ-loop}}$ is the value for the limit of the content of the γ-loop in the Fe binary phase diagram. The values were evaluated by thermodynamic calculation, using the application ThermoCalc and the database SSOL.

*2: The values are quoted from the Fe binary phase diagram.

*3: The gradient of transformation temperature per unit content for the Fe-0.1mass%M binary alloy, where M is the alloying element. The $k_{A4}$ and $k_{A3}$ are the gradients for $A_{\text{f}}(\gamma/\delta)$ and $A_{\text{f}}(\gamma/\alpha)$ respectively. The values were evaluated by thermodynamic calculation.

*4: The values are the coefficients in the relationships:

$A_{\text{f}}(K)=1665+1122(%Cr)-60(%Si)+12(%Mn)-140(%P)+1460(%W)-7(%C)-37(%Mo)+62(%Sn)-47(%V)$

$A_{\text{f}}(K)=1183-203(%Cr)+50(%Si)+15.2(%N)+33.8(%)\text{Cu}+44.7(%)\text{Ni}+104(%)\text{V}+31.5(%)\text{Mo}+126(%)\text{Si}+700(%)\text{P}+400(%)\text{Al}+400(%)\text{Ti}+120(%)\text{As}$

where all the compositions are given in mass %.

The former is the relationship evaluated by Ueshima from the phase diagram. The latter is the empirical relationship quoted by Leslie.

*5: The equilibrium distribution coefficient. Each value corresponds to the ratio of the solute content in the δ phase to that in the liquid phase for the Fe-0.1mass%M binary alloy, evaluated from the equation: $k^{\text{L}}=C^\delta/C^\text{L}$, by thermodynamic calculation.

*6: The values are quoted from ref. 19.
illustrates the solidification mode in the Fe(0.15Si–0.6Mn, in mass%)–C–P pseudo-ternary system. The solidification mode is predicted to be hypo-peritectic in all the test steels with equilibrium compositions. Figure 2 shows that the P addition is also expected to lower the peritectic temperature range and to spread the temperature ranges of the L/delta H11001/delta H11001/g triplex phase and the delta+gamma H11001/g duplex phase, illustrating the Fe(0.15Si–0.6Mn–xP, in mass%)–C pseudo-binary systems.

Slabs with a thickness of 100 mm and a width of 800 mm were cast with a laboratory-scale vertical-type continuous caster, equipped with a secondary cooling zone by water spray, at Sumitomo Metal Industries Ltd./Corporate R&D Labs., Hasaki. Table 3 shows the casting conditions in the present study.

2.2. Macro- and Micro-structural Characterization

The specimens for characterization were sampled at 1.5–2.5 m in longitudinal distance from the bottom (the meniscus position where the withdrawal started in the continuous casting) of a 3.3 m-long continuously-cast slab and at a half or a quarter width of an 800 mm-wide slab. Figure 4 shows a diagram of the observed cross sections of the as-cast slab. Macrostructural observation was performed on the longitudinal cross section (L section). Microstructural observation was performed on both the L section and the cross section parallel to the 800 mm-wide surface (Z section). The Z section at 1.8 m in longitudinal distance from the bottom, a quarter of the width of 800 mm, and a quarter of the thickness of 100 mm in each as-cast slab will be designated as the analysis region. The specimens were etched to reveal the solidification structure and the gamma structure, respectively. The etching reagents were a saturated picric acid for the dendrite structure revelation and a nital or a mixture of picral and nital for the prior-gamma structure revelation.6,21)

Solidification structures were examined by both optical microscopy and EPMA. The secondary dendrite arm spacing, S2, was evaluated by the linear intercept method, by counting the numbers of arms over a given length of the primary arm, using the optical microscopic observation in the L section. The micro-segregation mapping image22,23) for solutes such as P and Mn was given by EPMA (at 15 kV–0.5 μA) for an area of 2.56 mm×2.56 mm in the analyses region. Data sets of point analysis with every 5 μm beam scanning for both x and y directions yielded 512 pixels×512 pixels images. A statistical analysis was carried

<table>
<thead>
<tr>
<th>Sample</th>
<th>C (mass%)</th>
<th>Si (mass%)</th>
<th>Mn (mass%)</th>
<th>P (mass%)</th>
<th>S (mass%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01P</td>
<td>0.108</td>
<td>0.160</td>
<td>0.576</td>
<td>0.010</td>
<td>0.003</td>
</tr>
<tr>
<td>0.10P</td>
<td>0.108</td>
<td>0.176</td>
<td>0.607</td>
<td>0.007</td>
<td>0.004</td>
</tr>
<tr>
<td>0.20P</td>
<td>0.104</td>
<td>0.169</td>
<td>0.592</td>
<td>0.197</td>
<td>0.003</td>
</tr>
</tbody>
</table>

Table 2. Chemical composition of test steels (in mass%).
out on the mapping image to evaluate the details of the dendrite structure, such as the morphology and the primary arm spacing. The image of the area fraction solid, $f$, was remapped according to the relative cumulative frequency (RCF) of the P or Mn intensity. Two secondary arm plates crossed each other at a right angle, in the mapping image of the area fraction solid. The center of the cross shape was regarded as the primary arm. The primary dendrite arm spacing, $S_1$, was evaluated statistically by the following square conversion:

$$S_1 = (A_p/n)^{0.5}$$

where $A_p$ is the observed area ($6.55 \text{ mm}^2$; $2.56 \text{ mm}$ square) in the $Z$ section with a mapping image of the area fraction solid and $n$ is the number of primary dendrite arms.

The grain size is evaluated by microscopic observation in the $Z$ section. Since the grain structure is columnar, the width of the columnar grain is defined as the grain size. The grain size, $d_g$, was also evaluated by the following square conversion:

$$d_g = (A_g/n)^{0.5}$$

where $A_g$ is the observed area ($14–36 \text{ mm}^2$) and $n$ is the number of prior-$\gamma$ grains. In the etched microstructure, film-like $\alpha$ grains were observed along the prior-$\gamma$ grain boundaries. Then the film-like $\alpha$ grains were used as markers for the prior-$\gamma$ grain boundaries.

3. Results and Discussion

3.1. Primary Solidification Structure ($\delta$ Dendrite)

Macroscopic primary solidification structures in the $L$ section of the continuously cast (CC) slabs are shown in Fig. 5. The columnar dendritic structure prevails from the surface to the center of the thickness in all the slabs. The dendritic morphology is seen more clearly in the 0.10P (Fig. 5(b)) and the 0.20P (Fig. 5(c)) than in the 0.01P (Fig. 5(a)).

Figure 6 shows the change of the secondary dendrite spacing $S_2$ along the thickness for each slab. The $S_2$ increases with an increase in the distance from the slab surface, and $S_2$ is almost equivalent in all the slabs. For example, the $S_2$ at a quarter thickness of the slab is approximately 130 $\mu$m. The cooling rate in low carbon steel during solidification can be estimated to be approximately 1.7 K/s by the following equation:

$$S_2 = 688(60 \cdot r)^{-0.36}$$

where $S_2$ is the secondary arm spacing in $\mu$m, and $r$ is the cooling rate in K/s. The secondary arm spacing in the 100 mm-thick slabs is between a third and a half and the cooling rate converted by Eq. (3) is estimated to be more than 10 times that in 250 mm-thick continuous casting slabs.

The mapping images of the area fraction solid in Fig. 7 clearly reveal the solidification morphology in the $Z$ section of the CC slabs; the primary crystal shows a typical dendritic morphology with light-gray colors. The light-gray colored cross structure, whose center is believed to be a primary dendrite arm, is observed clearly in each slab, especially in the 0.10P (Fig. 7(b)) and 0.20P (Fig. 7(c)). The dendrite morphology is affected by the P addition as mentioned below. A dark-gray colored line or a Mn-segregated zone with a high area fraction solid of more than 0.9 surrounds each dendrite cross in the 0.01P (Fig. 7(a)). The boundary is assumed to be the final solidification region in the peritectic reaction. On the contrary, the dendrite mor-
Phology is more complex in both the 0.10P (Fig. 7(b)) and the 0.20P (Fig. 7(c)). First, the plate-like dendrite structure tends to evolve by joining the secondary dendrite arms that branched off from the neighboring primary arms.24,27,30) Furthermore, some tertiary arms branched off from the secondary arms in the 0.20P (Fig. 7(c)). These complicated dendrite morphologies caused by the P addition are similar to the result from the previous study in the Fe–P alloy.31) However, the primary dendrite arm spacing $S_1$ evaluated by Eq. (1) is almost constant between 0.31 mm and 0.32 mm in each slab. Consequently, the P addition makes the dendrite structure complicated without changing the dendrite arm spacing, $S_1$ or $S_2$.

3.2. Secondary Structure ($\gamma$ Grain)

Macroscopic grain structures in the L section of the CC slabs are shown in Fig. 8. The columnar grain structure prevails throughout the thickness in the 0.01P and the 0.10P slabs. The prior-$\gamma$ grain morphologies are shown in Fig. 9, by tracing the grain-boundary-$\alpha$ grains in the L section of the slabs. The prior-$\gamma$ grain size is apparently smaller in the 0.10P (Fig. 9(b)) than in the 0.01P (Fig. 9(a)). Figure 10 shows the change of the $\gamma$ grain size $d_\gamma$ along the thickness, evaluated by Eq. (2). The high P steels, or 0.10P and 0.20P, have finer grain size, approximately half of that in the 0.01P throughout the thickness of the slab. The $d_\gamma$ in the 0.20P is almost equal to that in the 0.10P. For example, the grain size at a quarter thickness is 1.57 mm, 0.73 mm and 0.76 mm, respectively in 0.01P, 0.10P and 0.20P. In all the slabs,
$d_g$ increases with distance from the slab surface, in the same way as $S_1$ shown in Fig. 6, accompanied by a reduced cooling rate.

Figure 11 shows the comparison between $S_1$ and $d_g$. Since the initial $\gamma$ grain size without rapid growth is assumed to correspond to the primary arm spacing in the hypo-peritectic carbon steel, the coarseness of the $\gamma$ grain by rapid growth can be determined by the following equation:

$$n_c = \frac{d_g^2}{S_1^2} \quad \text{(4)}$$

where $n_c$ is the coarseness number. The number $n_c$ is approximately 5–6 in the 0.10P or 0.20P and 25–30 in the 0.01P. It is indicated by the $y$-axis on the right side of the graph in Fig. 11. Namely, high P steels have a fairly low $n_c$, a fifth that of the 0.01P.

Microscopic structures at a quarter thickness of the CC slabs in the L section and in the Z section are shown respectively in Figs. 12 and 13. The film-like $\alpha$ grains, assumed to be formed at the prior-$\gamma$ grain boundaries, are observed clearly in all the slabs. The Widmanstätten $\alpha$ grains are mainly observed in the prior-$\gamma$ grain. In the 0.10P (Figs. 12(b), 12(e), and 13(b)) and the 0.20P (Figs. 12(c), 12(f), and 13(c)), globular $\alpha$ grains are also dispersed in the prior-$\gamma$ grain. This is one of the characteristic changes caused by the P addition.

3.3. Effect of Segregation on Structure Evolution

The solidification mode in all the test steels is predicted to be similar or hypo-peritectic in the equilibrium compositions as illustrated in Figs. 2 and 3. However, P addition affects the as-cast structure considerably, and it causes the refinement of the $\gamma$ grains and the formation of dispersed globular $\alpha$ grains that are mentioned above. Next, we will discuss the effect of micro-segregation on the structure evolution.

Figure 14 shows the EPMA mapping images of the solutes in the Z section at a quarter thickness of the slabs. The observed areas shown in Fig. 14 correspond to that in Fig. 13. The C mapping image shows the final structure.
after the $\gamma/\alpha$ transformation. The C-poor (light-gray-colored) area corresponds to the $\alpha$ grains and the C-rich (dark-gray-colored) area to the cementite and grain boundaries. The C mapping images of high phosphorus slabs in Figs. 14(b) and 14(c) show globular grains dispersed in the prior-$\gamma$ grain. The globular grains are corresponding to the globular $\alpha$ grains in Figs. 13(b) and 13(c) and existing at the P-rich spots in the P mapping images of Figs. 14(b) and 14(c).

The Mn and P mapping images illustrate the primary structure that evolved during solidification as previously shown in Fig. 7. The dendrite cross structure is illustrated by the Mn-poor area with less than 0.55 mass% Mn for all the slabs. The cross structure is also illustrated by a relatively low P area with less than 0.15 mass% P for the 0.10P (Fig. 14(b)) or with less than 0.30 mass% P for the 0.20P (Fig. 14(c)). The intensive Mn segregation line, which surrounds the dendrite cross structure, can be observed only in the 0.01P (Fig. 14(a)). Meanwhile, the inter-dendritic segregation of Mn is fairly dispersed in the 0.10P (Fig. 14(b)) and the 0.20P (Fig. 14(c)). Several statistical analyses will be conducted to discuss the change of the Mn segregation...
behavior by the P addition in detail.

**Figure 15** shows the relationship between the area fraction solid, \( f \), or the relative cumulative frequency (RCF) and the concentration of solutes. The Mn concentration (\( C_{\text{Mn}} \)) is lower for the 0.01P than for the 0.10P and 0.20P below the \( \text{RCF}_{\text{Mn}} \) (RCF of the Mn intensity) of 0.9, but becomes higher for \( \text{RCF}_{\text{Mn}} \) above 0.9. The P concentration (\( C_{\text{P}} \)) increases much more rapidly for the 0.10P and the 0.20P than for the 0.01P when the \( \text{RCF}_{\text{P}} \) (RCF of the P intensity) is greater than 0.95. The maximum P concentration, which is defined as the concentration at the \( \text{RCF}_{\text{P}} \) of 0.995, is three times or more higher than the average composition in a steel, approximately 0.3 mass% for the 0.10P and 0.7 mass% for the 0.20P.

**Figure 16** shows the relationship between the P concentration and the Mn concentration in the 0.10P and the 0.20P. The \( C_{\text{Mn}} \) in Fig. 16 is defined as the arithmetic mean of the Mn concentration in the marginal distribution classified by \( \text{RCF}_{\text{P}} \). The \( C_{\text{Mn}} \) for each slab increases linearly with \( C_{\text{P}} \) and reaches a peak. Then it decreases slightly in the P-rich region after the peak. The \( C_{\text{Mn}} \) is higher for the 0.10P than for the 0.20P in the P concentration range from 0.1 to 0.3 mass%, where the distribution curves co-exist. The \( C_{\text{P}} \) is 0.26 mass% and 0.34 mass% for the 0.10P and the 0.20P, respectively when the \( C_{\text{Mn}} \) is at the peak. However, the \( \text{RCF}_{\text{P}} \) at the peak is higher for the 0.10P than for the 0.20P, or 0.99 and 0.90 for the 0.10P and the 0.20P, respectively. In short, there is a greater decrease in the Mn concentration in the P-rich region for the 0.20P. In Fig. 16 the coefficient of variation (CV) is also used to illustrate the extent of the dispersion of the Mn concentration. The CV is defined as the standard deviation divided by the arithmetic mean of the Mn concentration in the marginal distribution. The CV for each slab maintains a low value or is less than 0.1 until the \( C_{\text{Mn}} \) reaches the peak and then increases after the \( C_{\text{Mn}} \) peak. In other words, the Mn dispersion occurs in the P-segregated region.

**Figure 17** shows the change of the probability distribution of \( C_{\text{P}} \) and \( C_{\text{Mn}} \) according to the P content. The 2-dimensional P–Mn concentration map is meshed with 0.01 mass% in each solute. The probability density of each mesh is classified by the relative efficiency (RE), which is defined by the following:

\[
\text{RE}_{ij} = \frac{\sum F_{i}(\geq F_{ij})}{\sum F}
\]

where, \( ij \): the sub-script indicating the mesh number in the P–Mn concentration map

\( F \): the frequency of the mesh

\( \sum F_{i}(\geq F_{ij}) \): the sum of the frequencies which are larger than or equal to \( F_{ij} \)

\( \sum F \): the total sum of the frequencies that is equal to the sample population or 512² in the present study.

In other words, a randomly selected pixel from the micro-segregation map shown in Fig. 14 has a set of P and Mn concentrations with the probability distribution shown in Fig. 17. For the 0.01P, \( C_{\text{Mn}} \) spreads from 0.4 to 0.9 mass%. For the 0.10P and the 0.20P, the distribution of \( C_{\text{Mn}} \) becomes narrower from 0.4 to 0.8 mass% and the distribution of \( C_{\text{P}} \) spreads to a higher concentration range. These results clarify that the P addition affects the Mn segregation behavior in the present slabs, especially the dispersion of Mn in the final solidification region.

The behavior of the Mn distribution in high P slabs can
be explained from the three effects that occur from the bcc-stabilization. The first is that the peritectic reaction is prohibited by the P enrichment in the final solidification region. The g phase is shown to precipitate not in the peritectic reaction but in the d/g solid phase transformation. The second is that the enriched P stabilizes the d phase in a high temperature range after solidification. Manganese diffuses easily in the stabilized d phase,23,25) since the diffusion constant of Mn is much higher in the d phase than in the g phase.32,33) The third is that the redistribution of Mn occurs during the d/g transformation. The Mn segregation is reduced in the final solidification region, since the inter-dendritic P-rich spots retain the d phase and the Mn is partly redistributed from the d phase to the g phase.

Next, we will summarize the relationship between the micro-segregation and the solid phase transformation temperatures. Figure 18 shows the contour lines of equilibrium transformation temperatures, $A_{\gamma}$ (d/γ) and $A_{\alpha}$ (γ/α), in the Fe(0.10C–0.15Si)–P–Mn pseudo ternary system. With an increase in the P concentration, the $A_{\gamma}$ temperature decreases rapidly, while the $A_{\alpha}$ temperature increases gradually and indicates that the γ single phase temperature range ($A_{\gamma}$–$A_{\alpha}$) shrinks by the P concentration as illustrated in Fig. 1. As shown in Fig. 18(a) the high P concentration stabilizes the d phase and decreases the completion temperature of the d/γ transformation. The d/γ phase transformation range extends to a lower temperature due to the P addition, especially its segregation. For example, the tempora-
ture range is extended from 1700 K to lower than 1650 K for the 0.10P and from 1675 K to lower than 1500 K for the 0.20P by the segregation. There is a strong possibility that the δ phase is partially retained at the spots with a highly segregated P of above 0.6 mass% for 0.20P, as indicated by the right side of the dash-dotted lines in Fig. 18. In such a P-rich region, the transformation into a δ phase may not occur even in the low temperature range. Hence, the remaining δ spots may pin the γ grain boundary migration in the temperature range of rapid growth of the γ grain, for example, at temperatures higher than 1700 K. The pinning by δ spots prevents the γ grain from coarsening. This pinning effect remains in a lower temperature range due to the P segregation.

The high P segregation has also been proven to affect the δ grain evolution. The P enrichment stabilizes the bcc locally and may retain the δ phase or raise the γ′/α transformation temperature as shown in Fig. 18(b). Thus, the globular α grain shown in Fig. 13 has been shown to originate from an inter-dendritic P-rich spot or a predominant site for the γ′/α transformation.

Consequently, the phosphorus addition and its segregation affect the bcc stabilization and cause the refinement of the γ′ grain and the evolution of the globular α grain.

4. Conclusions

Slabs in 0.1 mass% C steels with phosphorus contents ranging from 0.01 to 0.2 mass% were continuously cast. Their primary solidification structures and secondary grain structures have been characterized.

(1) Phosphorus addition affects the dendrite morphology by producing a complicated structure but hardly affects the primary and secondary dendrite arm spacing.

(2) In the high phosphorus steels, the prior-γ structures are refined effectively. The γ′ grain size is almost half of that in the 0.01 mass% P containing steel.

(3) In the high phosphorus steels, the globular α grains evolve at the phosphorus-rich spots in the prior-γ grain.

(4) Phosphorus addition affects the manganese segregation by promoting the dispersion of manganese in the inter-dendritic region.

(5) These microstructures and manganese distribution are caused by the local stabilization of bcc at the inter-dendritic phosphorus-rich region which has a lowered A_{24} and an elevated A_{23}. The completion of the δ/γ transformation is remarkably suppressed by the phosphorous segregation. The retained δ phase can pin the γ grain growth effectively.

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