Microstructure of Cast Strip in 0.1 mass% C Steels Containing Phosphorus

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Cast strips of 0.1 mass% C steels with phosphorus contents ranging from 0.01 to 0.2 mass% have been produced by using a twin drum type continuous casting machine, and their microstructures have been characterized. Fine dendrite structure in the strips provides a fine dispersion of the segregated phosphorus regime. Phosphorus addition changes the $\alpha$ grain structure dramatically and decreases the $\gamma$ grain size. The EPMA (Electron Probe Micro Analyzer) mapping and the diffusion analysis of phosphorus in the $\gamma$ phase indicate the presence of a retained $\delta$ phase in the austenite temperature. The pinning effect of the $\delta$-ferrite on the $\gamma$-grain growth must be kept in the temperature range of the rapid $\gamma$ growth. The balance of strength and ductility for the cast strip is improved as the phosphorus content increases.

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1. Introduction

The development of a new steel making process without extra-refining of low-grade iron resources to reduce the by-products such as slags and CO$_2$ exhaust during the steel making process is desirable in the 21st century. The creation of \textit{ultra-steel} from low grade iron resources using novel processes such as continuous casting, strip casting and cross-rolling has been studied,\textsuperscript{1-3} because of the increase in the amount of steel scraps and because of the use of low grade iron ore.

Phosphorus is one of the major impurities in the process of iron smelting. High phosphorus steels are generally undesirable in steel making, since they show low toughness and poor weldability. Iron smelting also produces a large quantity of slags (by-products) expensing large amounts of resources and energy, especially when removing phosphorus. Grain refining by thermo-mechanical treatment has improved the balance of strength and toughness of the high phosphorus steels.\textsuperscript{2,3} Impurities such as P and Cu are not only effective in solid solution or precipitation strengthening, but also affect the final microstructure due to their segregation. Therefore, if the impurities are finely dispersed and the grain size is small, there are possibilities for overcoming the poor properties in some usages, even in low-grade steels.

Near net shape casting such as twin drum type strip continuous casting\textsuperscript{4} and thin slab continuous casting\textsuperscript{5,6} is the most promising processing method for developing a fine dispersion of micro-segregations due to rapid solidification. The twin drum type strip casting can save about 90% of the energy for the process from casting to hot rolling.\textsuperscript{7} In the present study, continuously cast 0.1 mass% C steels with or without phosphorus addition have been produced by the twin drum type strip casting, and their microstructures have been characterized. Effects of phosphorus on the solidification structure in the cast strips are discussed.

2. Experimental Procedures

2.1 Materials and casting conditions

Table 1 shows the chemical compositions of the three test steels produced by the twin drum caster at the Mitsubishi Heavy Industries Ltd., Hiroshima R&D Center. The chemical compositions are based on 0.1C-0.15Si-0.60Mn in mass%, and the alloying phosphorus content is in the range from 0.01 to 0.20, i.e. A: 0.01P, B: 0.10P and C: 0.20P.

Table 2 shows the casting conditions in the present study; the casting speed was 20 m/min, the casting temperature was 1843±20 K, the casting weight was 15 kg, and the mold width was 150 mm. The drum force controlled the thickness of cast strips with about 2 mm. The cast strips were radiantly cooled on the transportation rollers table.

2.2 Microstructure analyses

Dendrite structure and microstructure were observed by optical microscopy on the TD (transverse direction) plane of the cast strips. Chemical etching was done in a stirred solution with 1 g ferric acid $\times$ 100 mm$^3$ picric acid and 3 vol% nitric acid, respectively. The cast strips were cut into the longitudinal direction, the segregation quantity of the impurity phosphorus by the EPMA analysis was measured at the section, and the microstructure was observed by an optical microscope. The setting condition of EPMA analysis was car-

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\begin{table}[h]
\centering
\caption{Material Contents (mass\%)}
\begin{tabular}{cccccc}
\hline
Material & C & Si & Mn & P & S \\
\hline
A & 0.11 & 1.17 & 0.62 & 0.014 & 0.014 \\
B & 0.09 & 0.17 & 0.62 & 0.082 & 0.016 \\
C & 0.11 & 0.16 & 0.67 & 0.197 & 0.014 \\
\hline
\end{tabular}
\end{table}

\begin{table}[h]
\centering
\caption{Casting conditions for cast strips.}
\begin{tabular}{lcccc}
\hline
Mold type & Twin drum ($\phi$300 mm $\times$ W150 mm) \\
Casting weight & 15 kg \\
Deoxidation & Al-Si killed \\
Casting temperature & 1823–1858 K \\
Casting speed & 0.333 m/s \\
Casting control & Drum force control \\
\hline
\end{tabular}
\end{table}
ried out at 20 KV–1 µA on the TD plane, the pixel size was 2 µm in square, and the number of total pixel data, \( N_{\text{total}} \), was 250000. The number of pixel data containing phosphorus, \( N_p \), is defined as a function of phosphorus concentration every 0.02 mass\%P.

The tensile test of the cast strips was done at ambient temperature in air at a strain rate of \( 5 \times 10^{-4} \) s\(^{-1} \) using a screw driven-type tester. Flat test pieces (JIS Z2201, No. 13-B type) were cut parallel to the casting direction, RD, for all steels; the gage length was 50 mm.

3. Results and Discussion

3.1 Dendrite structure and micro-segregation

Figure 1 shows the dendrite structure in the TD plane of cast strips A, B and C. Dendrites are well developed almost throughout the thickness regardless of the phosphorus content. Equiaxed crystals are not observed.

Figure 2 shows the dendrite arm spacing of steels A, B and C. The primary dendrite arm spacing, \( \lambda_1 \), is about 40 µm, and the secondary one, \( \lambda_2 \), is 10–20 µm for all 2 mm thick cast strips. The secondary dendrite arm spacing in the conventional slab is about 100–200 µm so that it is 10 times that of the cast strips. The cooling rate at the solidification is estimated from the secondary dendrite arm spacing:

\[
\lambda_2 = 688(60 \cdot R)^{-0.36}(\mu m)
\]

where \( R \) is the growth rate (K/s).\(^{4)}\) The cooling rate of the strips is about 800 K/s and is about 400 times that of the slab.

Figure 3 represents the EPMA line analysis profile of the phosphorus concentration for steels A, B and C. Phosphorus segregation appears clearly. The higher the phosphorus content is, the higher the segregation peak of the phosphorus concentration is (Fig. 3(a)). The peaks are mostly detected at a distance of every several ten \( \mu \)m so that they are fitted to the primary dendrite arm spacing. Thus rapid solidification is very effective for a fine dispersion of the phosphorus segregation. Each profile shows a normal distribution, which may be reflected from the practical partition coefficient of phosphorus (Fig. 3(b)). Most of the distributed phosphorus may be maintained through solid-solid transformations. The second peaks appear in the range of about 0.6 mass\%P for the steels B and C. The number of pixels, \( N_p \), in 0.55 mass\%P or over, is about 1% of the total pixels number, \( N_{\text{total}} \) for the steel C.
where \( l_{\text{ave}} \) (\( \mu \text{m} \)) is the average distance between the adjacent maxima and minima, and \( D_s \) (\( \text{mm}^2/\text{s} \)) is the diffusivity of the solute in the solid.

We assume that the diffusion length \( l_{\text{ave}} \) is equal to half of the primary dendrite arm spacing (Fig. 5). Relevant data for the diffusivity of carbon, phosphorus, and manganese in austenite are given as:

\[
Q_s = \text{Activation energy (J/mol)}
\]

\[
t_r = \exp \left( \frac{Q_s}{RT} \right) \int_{t_1}^{t_2} \exp \left( -\frac{Q_s}{RT} \right) dt
\]

(2)

where \( t_1 \) and \( t_2 \) are the limits of integration.

It is reasonable to regard the micro-segregations in the cast structures as periodic in Fig. 5, and to only consider the peak concentration, \( C_{\text{max}} \). The extent of the solute diffusion is evaluated by:

\[
\frac{C(t_r) - C_{\text{ave}}}{C_{\text{max}} - C_{\text{ave}}} = \exp \left( -\pi^2 D_s l_{\text{ave}}^2/4 \right)
\]

(3)

\[
D_s = D_0 \cdot \exp \left( -\frac{Q_s}{RT} \right)
\]

(4)

Fig. 3 EPMA analyses for phosphorus concentration in the cast strips: (a) line profiles, and (b) frequency proportion.

3.2 Solute diffusion during continuous cooling

Figure 4 shows a part of the pseudo-binary phase diagram of Fe–0.1C–0.15Si–0.60Mn–P (in mass%). The \( \delta \)-ferrite is retained in the austenitic phase region even in the equilibrium condition, if the phosphorus content is above 0.55 mass%.

The micro-segregation of phosphorus was clearly detected in the above diagram. However, the equalization of micro-segregations occurred through diffusion during the cooling of the cast strip. Thus, the diffusion of segregated solutes was evaluated to clarify whether or not the \( \delta \)-ferrite was retained in the austenitic phase region.

The extent of this diffusion is expressed in terms of an equivalent isothermal homogenization time, \( t_r \), at a chosen reference temperature, \( T_r \). If \( Q_s \) denotes the activation energy (J/mol) for the diffusion of the solute in the solid, the \( t_r \) at \( T_r \) is given by:

Fig. 4 Pseudo-binary phase diagram of Fe–0.1C–0.15Si–0.60Mn–P (in mass%).

Fig. 5 Diffusion model applied to continuous cooling.

Fig. 6 Estimated continuous cooling curves from liquidus to 973 K for the 0.1C–0.15Si–0.60Mn–0.2P (in mass%) steel.

where \( l_{\text{ave}} \) (\( \mu \text{m} \)) is the average distance between the adjacent maxima and minima, and \( D_s \) (\( \text{mm}^2/\text{s} \)) is the diffusivity of the solute in the solid.

We assume that the diffusion length \( l_{\text{ave}} \) is equal to half of the primary dendrite arm spacing (Fig. 5). Relevant data for the diffusivity of carbon, phosphorus, and manganese in austenite are given as:

Fig. 6 Estimated continuous cooling curves from liquidus to 973 K for the 0.1C–0.15Si–0.60Mn–0.2P (in mass%) steel.
where the universal gas constant \( R \) is 8.314 (J/(mol·K)).\(^9\)

Figure 6 shows the calculated cooling curve at 1/4 of the thickness depth of the steel C. We assume that the average heat flux from the molten metal to the copper mold cooled by water is \( 7 \times 10^6 \) W/m\(^2\). We apply the Temperature Recovery Methods\(^10\) to estimate the temperature of the strip casts. Physical properties of pure iron are used, and the liquidus (\( T_L \)) and the solidus (\( T_S \)) temperatures are given as follows:\(^11\)

\[
T_L(K) = 1809 - (78(%C) + 7.6(%Si) + 4.9(%Mn) + 34.4(%P) + 38(%S) + 4.7(%Cu) + 3.1(%Ni) + 1.3(%Cr) + 3.6(%Al))
\]

\[
T_S(K) = (\text{solidus temperature of Fe–C binary phase diagram}) - (20.5(%Si) + 6.5(%Mn) + 500(%P) + 700(%S) + 1(%Cr) + 11.5(%Ni) + 5(%Al))
\]

We obtained the relationship between \( t \) and \( T \) from the calculated curve. The actual transformation temperatures at \( t_1 = 1743 \) K and \( t_2 = 973 \) K are reached after 0.15 and 28.5 sec, respectively. If 1473 K is used as a reference temperature, numerical integration of eq. (2) gives:

\[
t_{1473}(C) = 7.5 \text{s}, \quad t_{1473}(P) = 11.3 \text{s}, \quad t_{1473}(Mn) = 18.0 \text{s}
\]

Then the extent of the solute diffusion is evaluated from eq. (3) as a function of the primary dendrite arm spacing by inserting the diffusivities of C, P and Mn at 1473 K.

Figure 7 shows the relationship between the primary dendrite arm spacing and the extent of diffusion for carbon, phosphorus and manganese in the steel C. Figure 9 shows the microstructure of the cast strips. Phosphorus addition changes the \( \alpha \)-grain structure dramatically. Grain boundary ferrite and Widmanstätten ferrite appear in the steel A. On the other hand, only polygonal ferrite is observed in the steel C. Both polygonal and acicular ferrites are detected in the steel B. These differences in the ferrite structure may depend on the nucleation and the growth of ferrite grains. Phosphorus addition also changed the \( \alpha \)-grain structure dramatically in the slabs where the globular \( \alpha \) grains in the prior \( \gamma \) grain appeared for the high phosphorus steel.\(^1\)

Rapid solidification is thought to be effective for developing the polygonal ferrite structure in the high phosphorus steel, since it promoted the retained \( \delta \)-ferrite in the austenite regime.

The prior austenite grain boundaries and inclusions generally provide the nucleation sites for the \( \alpha \)-ferrites. However, the retained \( \delta \) in the \( \gamma \) phase may provide a predominant site for the \( \gamma/\alpha \) transformation in the high phosphorus steel, since phosphorus stabilizes the \( \delta \)-ferrite and lowers the transformation temperature from \( \delta \) to \( \gamma \). The prior austenite and ferrite grain boundaries lie between the dendrite pits (Fig. 10). The dendrite pits reflect on the interdendritic micro-segregation regime, where the phosphorus concentration is higher than the average.

Therefore, the \( \delta \) ferrite formed in the interdendritic spaces must be retained to prevent the austenite grain growth for the steels B and C. Then the retained \( \delta \)-ferrite may provide a site
for the growth of the $\alpha$-ferrite grains.

### 3.4 Mechanical properties

Figure 11 summarizes the tensile properties of the cast strips. Yield phenomena did not appear in the strips. Both the ultimate tensile strength and the total elongation increase as the phosphorus content increases. However, the 0.2% proof stresses in all the cast strips are almost the same. Although the steel A showed less strain hardening, both the steels B and C showed a much higher strain hardening rate and good uniform elongation. Therefore, phosphorus addition with 0.1 mass% is effective for designing a good balance between the strength and the ductility in the cast strip.

![Microstructure of the cast strips in the longitudinal section](image)

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**3. Conclusions**

Cast strips of 0.1 mass% C steels with phosphorus contents ranging from 0.01 mass% to 0.2 mass% have been produced.
with a twin drum type continuous casting machine, and their microstructures have been characterized. Phosphorus is useful for providing a fine solidification structure and for improving the tensile properties in the cast strip as follows.

(1) The primary dendrite arm spacing was about 40 µm and the secondary dendrite arm spacing was about 20 µm. The twin drum type continuous casting is very effective for refining the solidification structure of the low C steels.

(2) The phosphorus segregated in the inter-dendrites regions where its concentration reached up to about 0.55 mass% in steel C. Thus rapid solidification is very effective for the fine dispersion of the P segregation.

(3) Phosphorus addition decreased the γ grain size. The γ grain size in the steel containing over 0.1 mass%P is about half of that in the steel without P addition. The δ ferrite phase formed in the interdendritic spaces may be retained and prevent the austenite grain growth.

(4) Phosphorus addition dramatically changes the α grain structure from a Widmanstatten ferrite to a polygonal one.

(5) The balance of strength and ductility for the cast strip has improved with the above 0.1 mass%P addition. Therefore phosphorus addition in the cast strip for low carbon steel has a big advantage as ecomaterial and ecological process, since strip continuous casting is the most promised process from the view points of near net shape metallurgy and energy saving.

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