Influence of Phosphorus Micro-Segregation on Ferrite Structure
in Cast Strips of 0.1 mass% C Steel

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Cast strips of 0.1 mass% C steel with or without phosphorus addition have been characterized by electron back-scattering diffraction pattern (EBSP) measurements. Then the formation of globular ferrite structure was discussed. EBSP analysis combined with optical microscopy clearly showed that a globular grain was fitted to be an α-ferrite grain. The EBSP analysis suggested that the retained-δ grain grew predominantly in the γ-grain and formed the globular α-ferrite during cooling. The microtexture in the globular ferrite structure depended highly on the solidification structure. It is important to scatter the primary dendrite growth direction into neighboring areas to develop fine prior-γ and α structures for the cast strip of high-phosphorus steel.

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1. Introduction

The development of a new steel making process that excludes the extra-refinement of low-grade iron resources that is used to reduce the by-products such as slags and CO₂ exhaust is desirable in the 21st century.¹¹ Phosphorus is one of the major impurities in the process of iron smelting, since segregated phosphorus causes low toughness and poor weldability. Near net shape casting²–⁵ such as twin drum type strip continuous casting⁶–⁸ and thin slab continuous casting is the most promising process for developing a fine dispersion of micro-segregations due to rapid solidification. The strip casting can save about 90% of the energy for the process from casting to hot rolling.¹¹ In the previous paper,⁹ cast strips of 0.1 mass% C steels with phosphorus contents ranging from 0.01 mass% to 0.2 mass% were produced with a twin drum type continuous casting machine, and their microstructures were characterized. Since the phosphorus segregated in the inter-dendrite regions, rapid solidification was very effective for its fine dispersion. Furthermore, the phosphorus was useful for providing a fine solidification structure, for decreasing the prior-γ grain size, and for improving the tensile properties in the cast strip. Therefore, if the impurities are finely dispersed and the prior-γ grain size is small, there are possibilities for overcoming the poor properties in some usages, even in low grade steels.

The electron probe microanalysis and the diffusion analysis of phosphorus for the cast strips indicated the presence of a retained δ phase in the austenite temperature.⁹ The retained δ-ferrite must prevent the austenite grain growth, and may provide a site for the growth of the α-ferrite grains. As a result, the phosphorus addition changed the morphology and the size of the α grain. Although the differences in the α-ferrite structure must depend on the nucleation and growth of the α-ferrite grains, the mechanism for developing a globular ferrite structure in the high phosphorus cast strip has not been very clear. Therefore, the crystal orientation of the α-ferrite grains was characterized by using electron backscattering diffraction pattern (EBSP) measurements⁹ in the present study to clarify the formation of the globular ferrite structure.

2. Experimental Procedures

2.1 Materials and casting conditions

Three 0.1 mass% C steels, i.e. 0P, 0.1P and 0.2P, produced by a twin drum caster in the previous study⁹ have been characterized. The alloying phosphorus content is different among them. Their chemical compositions are 0P: 0.11 C, 0.17 Si, 0.62 Mn, 0.014 P, 0.014 S; 0.1P: 0.09 C, 0.17 Si, 0.62 Mn, 0.082 P, 0.016 S; and 0.2P: 0.11 C, 0.16 Si, 0.67 Mn, 0.197 P, 0.014 S in mass percent. The cast strips have a thickness of about 2 mm and a width of about 150 mm. The casting conditions are described in detail in the previous paper;⁹ the casting speed was 20 m/min. The copper rolls were water cooled internally, and their surface was fully covered with a dimple pattern to scatter each primary dendrite growth direction against the normal direction, ND, as shown in Fig. 1.

2.2 SEM-EBSP measurements

The samples were cut from the center part of the cast strips into sections and then longitudinally for metallurgical observations. The longitudinal sections (transverse direction,
TD plane) were polished mechanically and electrically. The mechanical preparation was made on the colloidal SiO$_2$ (0.05 μm in diameter) suspension. Chemical etching for the dendrite and prior-$\gamma$ structures was first completed in a stirred solution with 1 g ferric acid and 100 mm$^3$ picric acid. A conventional electrical jet polishing was carried out in a stirred solution of 5% perchloric acid and 95% acetic acid at about 290 K with 80 V to remove the deformed subsurface layer and the pits on the sample surface. Chemical etching was also performed with 3% nitric acid to reveal the microstructure. The ferrite grain structure was observed with an optical microscope, and the area was marked by Vickers indentations. The electrical polishing was performed slightly again to remove the steps by etching. Then EBSP measurements were obtained with scanning electron microscope (SEM) to determine the crystal orientations of the bcc-ferrite grains. A half of the thickness was used for the analysis region since the dendrites were well developed almost throughout the thickness as shown in Fig. 1. A JEOL JSM-6400 microscope equipped with a LaB$_6$ type gun was employed at 20 keV. A data set of point analyses with every 2 μm beam scanning in hexagonal grid yielded the image and orientation maps characterizing the $\alpha$-ferrite grain structure.

3. Results and Discussion

3.1 Austenite and ferrite grain structures

Figure 2 shows the optical microstructure and the region for EBSP measurements for the samples, 0P and 0.2P. The microstructure is in the as cast state after cooling in air. Phosphorus addition changes the $\alpha$-structure dramatically. The 0.2P consists of only globular ferrite, although grain boundary ferrite and acicular or Widmanstätten ferrite are visible in the 0P. The average prior-$\gamma$ size for 0P and 0.2P was 300 μm and 90 μm, respectively.

Figure 3 shows EBSP maps in the TD plane for the 0P. Equiaxed and/or plate-like ferrites along a prior-$\gamma$ grain boundary show a similar crystal orientation amongst each other. Acicular ferrites nucleated from a prior-$\gamma$ grain boundary also show the same crystal orientation. Thus the prior-$\gamma$ grain boundary provides a predominant nucleation site for the $\gamma$-$\alpha$ transformation in the cast strip, 0P. Widmanstätten ferrites indicating the same crystal orientation appear in the prior-$\gamma$ grain. Their morphology is like a packet in the martensite structure, and they may keep the Kurdjumov-Sachs (K-S) relationship. The distribution of low quality EBSP data (black color in Fig. 3(b)) exhibits the martensitic structure. Measurements with higher resolution using FE-SEM are necessary to clarify their crystal orientation.

On the other hand, only globular grains appear for the 0.2P as shown in Fig. 4. They are almost aligned along the primary dendrite growth direction, and there is no indication of an existing grain boundary ferrite. Figure 5(a) shows a combined microstructure for the 0.2P where both grain boundaries and dendrite pits are revealed. The size and morphology of globular grains are fitted to those of prior-$\gamma$ grains in Fig. 5(a). Few small angle boundaries in the prior-$\gamma$ grains are detected in Fig. 4(b), and the misorientation angles of the sub-boundaries are mostly less than 1 degree. These facts suggest that the globular grain is also an $\alpha$-ferrite grain.

A strong texture near the $\langle 100 \rangle$ || ND appears in Fig. 4(c). The texture reflects the dendritic growth along the $\langle 100 \rangle$ crystal direction, since the primary dendrite growth direction is roughly parallel to the ND as shown in Fig. 1. The details will be discussed in section 3.3.

3.2 Globular ferrite generation

The $\delta$-ferrite is retained in the $\gamma$ 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 inter-dendrite regions for the 0.1P and 0.2P, and the dendrite pits in Fig. 5(a) reflect on the interdendritic micro-segregation regime. The diffusion analysis showed that the concentration gradients of segregated phosphorus were largely maintained down to the $A_3$ temperature where the $\gamma$ to $\alpha$-ferrite transformation occurred. Thus, the $\delta$-ferrite that formed in the interdendritic spaces must be retained to prevent the $\gamma$ grain growth for the casts 0.1P and 0.2P. The illustration in Fig. 5(b) gives an explanation of the globular $\alpha$ structure development, where the prior-$\gamma$ or $\alpha$ grain boundaries lie between the dendrite pits.
The solidification mode may be δ-solidification and not involve peritectic reaction. Although the liquid and/or δ-ferrite in the interdendritic spaces prevent the γ grain growth at around δ-γ transformation temperature, the neighboring γ grains that show almost the same crystal orientation must be coalesced and grew. Thus, several dendrite pits in a prior-γ grain can be seen in Fig. 5(a).

Furthermore, phosphorus increases the $A_3$ temperature. The retained-δ in the γ phase can also provide a predominant site for the γ-α transformation in the high phosphorus steel (Fig. 5(b)), since the region around the δ-ferrite has higher phosphorus content and may show a higher $A_3$ temperature.

Fig. 3 EBSD measurements for the area indicated in Fig. 2(a): (a) image quality map, and (b) orientation map to the ND with tiled inverse pole figure (IPF) (c). Black color in image (b) corresponds to the positions of large grain boundaries or low quality pixels (strained region).

Fig. 4 EBSD measurements for the area indicated in Fig. 2(b): (a) image quality map, (b) IPF map to the ND, and (c) 100 pole figure. Black colored lines in image (b) correspond to the positions of large grain boundaries. White colored lines in image (b) show small misorientation angles between 1 and 5 degrees.
than the other $\gamma$ phase regions. Not only acicular $\alpha$ ferrites but also globular $\alpha$ grains in the prior-$\gamma$ grain appeared for the continuously cast steels with high phosphorus. The cooling rate of the cast strips was much higher than that of the slabs. Thus, the growth rate of $\delta$-ferrite may be sufficient to make $\gamma$ transform $\alpha$ before the $\gamma$ grain boundaries become active for providing the $\alpha$-ferrite nucleation. In fact, the EBSP analysis suggests that the retained-$\delta$ ferrites grow predominantly in a $\gamma$-grain and form $\alpha$-ferrite sub-grains. The retained-$\delta$ ferrites in the prior-$\gamma$ grain may have the same orientation, and $\alpha$ sub-grain boundaries in Fig. 5(a) may exhibit carbon segregation. Therefore, the globular $\alpha$-grain structure is almost equal to the prior-$\gamma$ grain one.

3.3 Influence of solidification structure

Figure 6 shows the fiber texture diagram for regions 1–3 in Fig. 4(a), which displays the measured orientation distribution function, $f(g)$, along the $\alpha$ fiber with $\langle 110 \rangle$ parallel to the casting direction, RD, the $\gamma$ fiber with $\langle 111 \rangle$ planes parallel to the strip surface (i.e., their poles parallel to the ND), and the $\eta$ fiber with $\langle 100 \rangle$ parallel to the RD. In region 1, the globular grains are aligned very well along the primary dendrite growth direction and have almost the same crystal orientation. The grain size is larger (Fig. 4(b)), and the value of $f(g)$ in region 1 is higher around $\langle 100 \rangle - \langle 110 \rangle$ (Fig. 6(a)). Region 2 is in the initial dendrite growth zone and shows a finer grain structure with various crystal orientations (Fig. 4(b)). The value of $f(g)$ in region 2 is somewhat weaker in the $\alpha$ fiber. Region 3 corresponds to the coarsened ferrite grain structure in the dendrite growth zone along the ND. Region 3 is virtually free of texture where the fiber curve is close to unity (Fig. 6(c)). Therefore, the microtexture in the globular ferrite structure may depend highly on the solidification structure.

Figure 7 shows EBSP maps on the TD plane from the strip surface to the center for the 0.1P. The microstructure is classified into three zones, i.e., chill, complex dendrite and dendrite (Fig. 7(a)). These zones correspond to the initial, steady growth, and final solidification stages, respectively. As shown in Fig. 1, the directions of the dendrite growth are scattered in the cast strips. The $\alpha$ grains in the complex dendrite zone are smaller than those in the other zones. The neighboring $\gamma$ grains may have enough misorientation to prevent their growth, since dendrite growth directions are different. In the dendrite zone, the growth rate is lowered and the dendrite growth directions are almost parallel to the ND.
As a result, the pinning effect of the \( \gamma \)-ferrite on the \( \gamma \)-grain growth may be lost in the \( \delta \)-\( \gamma \) transformation. The \( \gamma \)-grain can also grow into neighboring areas, since the crystal orientations of neighboring \( \gamma \) grains are almost the same. Therefore, it is important to control the primary dendrite growth direction for the cast strip of high-phosphorus low-carbon steel to develop fine prior-\( \gamma \) and \( \alpha \) structures.

4. Conclusions

The crystal orientation of the \( \alpha \)-ferrite grains in the cast strips of 0.1 mass% C steels with phosphorus contents ranging from 0.01 mass% to 0.2 mass% has been characterized by using EBSP measurements. Then the formation of globular ferrite structure was discussed as follows:

1. Each globular grain that was fitted to a prior-\( \gamma \) grain was determined to be an \( \alpha \)-ferrite grain. Few small angle boundaries were detected in the globular grains, and the misorientation angles of the sub-boundaries were mostly less than 1 degree.
2. The EBSP analysis suggested that the retained-\( \delta \) grains grew predominantly in the \( \gamma \)-grain and formed the globular \( \alpha \)-ferrite grain during cooling.
3. The microtexture in the globular ferrite structure depended highly on the solidification structure. It is important to scatter the primary dendrite growth direction into neighboring areas for the cast strip of high-phosphorus low-carbon steel to develop fine prior-\( \gamma \) and \( \alpha \) structures.

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