Effects of Cr Addition on Coarse Columnar Austenite Structure in As-Cast 0.2 mass% Carbon Steel

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(Received on April 12, 2010; accepted on July 15, 2010)

Effects of Cr addition on as-cast Coarse Columnar austenite Grain (CCG) structure were investigated for 0.2 mass% carbon steel by means of rapid unidirectional solidification method which realizes cooling conditions similar to those in the vicinity of continuous cast slab surface. Although the as-cast structure of the unidirectionally solidified samples always consisted of the CCGs regardless of Cr addition, the aspect ratio of the CCGs was remarkably reduced by the Cr addition. During solidification, Fine Columnar austenite Grains (FCGs) existed at the growing front of the CCG region and the migration velocity of the FCG/CCG boundary was reduced by the Cr addition. EPMA analysis revealed that the Cr addition enhances P segregation at interdendritic positions, which lowers a temperature for completion of γ transformation, Tγ. This lowered Tγ reduces the migration velocity of the FCG/CCG boundary and, as a result, induces the formation of CCGs having shorter major axis diameters.

KEY WORDS: carbon steel; solidification; peritectic transformation; austenite grain; columnar structure; chromium; phosphorous; segregation; grain growth.

1. Introduction

As-cast γ-austenite grain size in peritectic carbon steels is one of the important parameters which determine the ductility of Continuous Cast (C.C.) slabs. Surface cracking susceptibility of the C.C. slabs depends largely on the as-cast γ grain size. It was reported that the surface crack propagates on the boundary of Coarse Columnar γ Grain (CCG) formed from the surface toward the center of the thickness and, moreover, the depth of surface crack is affected by the major axis diameter of CCG.1–3) Therefore, it is very important to prevent the formation of CCG structure in order to avoid the surface cracking. However, the formation process of CCG structure remains to be clarified.

The grain growth of γ phase in peritectic carbon steels immediately occurs after liquid or δ-ferrite phase disappears below a temperature for completion of γ transformation, Tγ, since the liquid or δ phase acts as a pinning phase for γ grain growth above Tγ.4–6) Some members in our group investigated the formation process of CCG structure in a hyperperitectic carbon steel during slow cooling solidification by means of Bridgman type unidirectional solidification method.7) It was observed that the CCG region develops along the direction of temperature gradient. Importantly, it was found that Fine Columnar γ Grain (FCG) always forms at the front of the CCG region and, moreover, the FCG region corresponds to the liquid+γ two phase field. The minor axis diameter of FCG is comparable to the primary dendrite arm spacing. Based on these observations, in the study on the γ grain growth of low carbon steels,8,9) a classical grain growth model based on curvature driven growth was applied to the prediction of CCG size with the assumption that the grain growth continuously takes place from the FCG to CCG at temperatures below Tγ. Although it was demonstrated that such a classical model is quite useful in predicting the γ grain size, the assumption of the continuous grain growth from the FCG to CCG remains to be verified. In our recent report,10) the formation process of CCG structure during metal mold casting of hyperperitectic carbon steels was investigated by means of a rapid unidirectional solidification method which realizes a cooling condition quite similar to that for a part near the slab surface of a practical continuous casting process. It was found that the FCG region forms at the front of CCG region also in case of the metal mold casting. The temperature at the boundary between the FCG and CCG regions corresponded to Tγ. Importantly, it was revealed that the continuous growth from the FCG to the CCG does not occur and, instead, the CCG region, which initially forms near the mold side, develops along the direction of temperature gradient by consuming the FCG region. Therefore, at a fixed point of the cast sample, the grain size discontinuously changes by about one order of magnitude from the FCG to the CCG when the temperature at the fixed point falls below Tγ, which is in marked contrast to the above-mentioned assumption in the continuous grain growth model.8,9) It was concluded in our
recent report that it is important to prevent the continuous development of CCG region along the direction of temperature gradient in order to realize the refinement of as-cast γ grain structure.

According to the studies on the effects of alloying elements on the as-cast γ structure, the addition of alloying element such as P and Al is quite effective in the refinement of as-cast γ structure. It was reported that the simultaneous addition of Al and P, both of which are known as ferrite-stabilizing elements, is effective in refining the CCG structure in 0.2 mass% carbon steel. This refinement originates from the pinning effect of δ-ferrite or liquid phases stabilized at lower temperatures due to the segregation of these elements. In this study, we focus on the addition of Cr which is also known as one of the ferrite-stabilizing elements. Cr is practically utilized as an alloying element which improves corrosion and wear resistances of steel. However, the effects of Cr addition on the as-cast γ structure have not been clarified in detail. Therefore, in this study, we investigate the effects of Cr addition on the as-cast γ structure in 0.2 mass% carbon steel.

2. Experimental Procedures

A 0.2 mass% carbon steel rod with a diameter of 26 mm was used as a row material. A piece of steel bar was placed in a MgO crucible with an inner diameter of 28 mm and a depth of 70 mm. Granular Cr (99.7 mass%) was placed in the MgO crucible together with the steel bar. The total weight of the sample was about 180 g. The composition of the samples used in this study is shown in Table 1. The samples without Cr addition and with 3 mass% Cr addition are called 0.2C and 0.2C+3Cr samples, respectively, in this paper. Each sample was melted at 1570°C in a SiC furnace filled with a five-nine pure Ar gas and held at the temperature for 1 h, followed by casting the melt into the rapid cooling unidirectional solidification equipment shown in Fig. 1. This equipment consists of a MgO pipe and a water cooled copper mold. The MgO pipe was preheated to 1570°C and was placed on the water cooled copper mold just before casting in order to realize upward unidirectional solidification. Especially, this equipment enables detailed investigation of the formation process of the microstructures during and after solidification by dropping the sample together with the MgO pipe very quickly into an iced water bath at predetermined timings after casting. In our preliminary experiment, the cooling rate just after solidification in the present sample was measured to be about 10°C/s at a point in the sample 10 mm away from the copper mold. This is quite comparable to that in the practical C.C. slab with the similar composition. The as-cast sample has a columnar shape with a height of 40 mm and a diameter of 28 mm. The ingot was sectioned vertically through the center axis of the columnar sample and the cross section was polished. The as-cast γ structure and the dendrite structure were observed after the etching with 3%-nital and Oberhoffer’s solutions, respectively.

In addition to the samples cooled to Room Temperature (RT), the observations were carried out for the samples quenched when predetermined periods (10–100 s) past after casting in order to clarify the formation process of the γ structure during casting. An Electron Probe Micro Analyzer (EPMA) was employed to analyze the concentration distribution of elements in the quenched sample.

3. Results and Discussion

3.1. Microstructures of the As-cast Samples

Figures 2(a) and 2(b) show the as-cast γ structure and the dendrite structure in the 0.2C sample cooled to RT, respectively. The bottom side of these figures corresponds to the mold side of the ingot. The bright lines in Fig. 2(a) represent the as-cast γ grain boundaries which are visible because of primary ferrite phase precipitating on the former γ grain boundary. It is seen that the CCG with a minor axis diameter of a few mm develops from the mold side toward the upper side of the cast sample. The aspect ratio of the CCGs in this sample was measured to be 4.6 on average. In Fig. 2(b), the columnar dendrites develop from the mold side toward the upper side of the sample. From the microstructural observations, unidirectional growth of the dendrite was confirmed over the whole observation area.

Figures 3(a) and 3(b) show the as-cast γ structure and the dendrite structure in the 0.2C+3Cr sample cooled to RT, respectively. The γ grain structure is not observed very clearly in the figure in this case because the addition of Cr suppressed the formation of the primary ferrite phase on the former γ grain boundary. For the visual aid, accordingly, the as-cast γ grain boundaries were traced based on the direct microscopic observation of the sample and drawn in Fig. 3(c). The dendrite structure in the 0.2C+3Cr sample is quite similar to that in the 0.2C sample. However, the addition of Cr leads to the change in the as-cast γ structure. A lot of equi-axed grains are seen together with the CCGs. The CCGs in this sample have much shorter major axis diameter than the sample shown in Fig. 2(a). The average aspect ratio of CCGs in the 0.2C+3Cr sample was measured.

Table 1. Chemical composition of the samples employed in this study.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Steel composition, in Mass%</th>
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<tbody>
<tr>
<td></td>
<td>C</td>
</tr>
<tr>
<td>0.2C</td>
<td>0.20</td>
</tr>
<tr>
<td>0.2C+3Cr</td>
<td>0.19</td>
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to be 2.0, which is much smaller than 4.6 in the 0.2C sample.

### 3.2. Development of CCG Structure During Solidification

In our recent report,\textsuperscript{10} it was found that the FCG structure exists at the front of CCG region during solidification in metal mold casting. The temperature at the FCG/CCG boundary corresponds to $T_g$. Figure 4 shows the microstructures in the 0.2C and 0.2C+3Cr samples quenched at 20 s and 40 s after casting operation. The FCG structures are observed at the front of the CCG region in all the micrographs. It should be noted that the length of the FCG region is long in the 0.2C+3Cr sample compared with that in the 0.2C sample. Also, the length of the CCG region measured from the mold side, $L_{CCG}$, is reduced by the Cr addition. Figure 5 shows the time dependence of $L_{CCG}$ in 0.2C and 0.2C+3Cr samples. In both samples, $L_{CCG}$ gradually increases with the increase in time. It is obviously shown that $L_{CCG}$ in the 0.2C+3Cr sample is always shorter than that in the 0.2C sample. In other words, the migration velocity of the FCG/CCG boundary is reduced by the Cr addition.

As mentioned above, the temperature at the FCG/CCG boundary corresponds to $T_g$ in the 0.2C samples.\textsuperscript{10} Figure 6 shows the phase diagram of Fe–0.2C–0.8Mn–0.2Si–0.02P–xCr (mass%) steel calculated by the CALPHAD method.\textsuperscript{14} One can see that the addition of 3 mass% Cr does not change $T_g$ substantially. However, it is considered that $T_g$ is
appreciably reduced at local regions of the structure, if the microsegregation of Cr occurs during the solidification process. Hence, we investigated Cr concentration profile across the dendrites. Figure 7(a) shows the dendrite structure in the CCG region and Fig. 7(b) shows the result of the EPMA analysis for Cr concentration. The bright parts in Fig. 7(a) correspond to the interdendritic regions. The line analysis for Cr concentration was performed between the points A and B in Fig. 7(a). It can be seen in Fig. 7(b) that the segregation of Cr occurs at the interdendritic regions. However, the degree of segregation is quite small. Therefore, the decrease in $T_g$ should not substantially occur only by the Cr segregation.

It was reported that Al addition to 0.2 mass% carbon steel enhances the P segregation at the interdendritic region during the solidification, and as-cast $\gamma$ structure was refined by the decrease in $T_g$ due to the P segregation. Fig. 8 shows the dependence of the partition coefficient of P between $\delta$-ferrite and liquid phases on Cr concentration. The partition coefficient was calculated for Fe–0.2C–0.8Mn–0.2Si–0.02P–$x$Cr (mass%).

Fig. 7. (a) Dendrite structure in the CCG region in 0.2C+3Cr sample quenched at 20 s. (b) Distribution of Cr concentration obtained by EPMA analysis between points A and B in Fig. 7(a).

Fig. 8. Effect of Cr addition on the partition coefficient of P between $\delta$ and liquid phases at 1500°C, calculated by CALPHAD method. The composition is Fe–0.2C–0.8Mn–0.2Si–0.02P–$x$Cr (mass%).
the liquid phase exists at lower temperatures, providing the pining effect on the migration of the FCG/CCG boundary. This should be the reason for the reduction of the migration velocity of FCG/CCG boundary by the Cr addition observed in Fig. 5.

3.3. Formation Mechanism of Relatively Equi-axed CCG Structure

In our recent report,\(^{10}\) it was found that the CCG region develops by consuming the FCG region. Figures 12(a)–12(c) show the schematic illustrations of this process. The bottom of the each illustration corresponds to the mold side of the sample. At temperatures above \(T_g\), the \(\gamma\) grains cannot grow due to the remaining liquid phase at the interdendritic regions, while the grains can grow at temperatures below \(T_g\). The large difference in grain size between FCGs and CCGs provides the large driving force for the development of CCG toward FCG region. Hence, the CCGs rapidly develop toward the FCG region immediately after the liquid phase disappears in the FCG region.

The mobility of the boundary between the FCG and CCG regions is an important parameter controlling the development of the CCG region. It is well known that the grain boundary mobility largely depends on temperature. The migration velocity of the FCG/CCG boundary, \(v_{\text{CCG}}\), the velocity of the development of CCG region should decreases with the decrease in the growth temperature. Therefore, if \(T_g\) is lowered, the temperature at the FCG/CCG boundary decreases and, accordingly, the migration velocity of the CCG region decreases. As mentioned above, \(T_g\) in 0.2C+3Cr sample was lowered locally at interdendritic regions by P segregation. Therefore in the 0.2C+3Cr sample, the large difference in grain size between FCGs and CCGs provides the large driving force for the development of CCG toward FCG region. Hence, the CCGs rapidly develop toward the FCG region immediately after the liquid phase disappears in the FCG region.

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From the previous studies,\(^{8,11–13}\) it has been known that the addition of some alloying elements such as P and Al leads to the decrease of \(T_g\) and the liquid phase does not exist in the FCG region. As shown in Fig. 13, a relatively large grain “A” grows in the FCG region, and it becomes the coarse grain. The driving force for the development of CCG toward FCG region significantly diminishes in the vicinity of the coarse grain “A” in FCG region. Then, the CCG does not grow along the long axis direction and, instead, the grain “A” becomes the coarse columnar shape and it finally grows into the CCG. Ahead of this CCG, the coarsening of a relatively large grain “A” will occur in the FCG region as shown in Fig. 13(c). This sequential formation of large grains in FCG region leads to the formation of CCGs having short major axis diameter in the 0.2C+3Cr sample. In fact, as shown in Fig. 14, it was observed that the relatively large grain exists in FCG region of the 0.2C+3Cr sample quenched at 20 s.

From the previous studies,\(^{8,11–13}\) it has been known that the addition of some alloying elements such as P and Al leads to the decrease of \(T_g\), and the refinement of CCG structure. In this study on the Cr addition, it was demonstrated that the decrease of \(T_g\) leads to the reduction of the migration velocity of the FCG/CCG boundary, and it results in the decrease in the major axis diameter of the CCGs. Therefore, it is considered that the lowering of \(T_g\) is effective not only in the refinement of CCG structure but also in the prevention of development of CCG structure at the surface of C.C. slab.
4. Conclusions

The early studies demonstrated that the addition of the ferrite stabilizing element such as P and Al refines the as-cast structure in peritectic carbon steels because of the pinning effect of $\delta$-phase. In this study, we investigated the effect of Cr, which is one of the ferrite stabilizing elements, on the as-cast structure in the 0.2 mass% C steel by using a rapid unidirectional solidification method. It was found that the addition of Cr yields the as-cast grain structure consisting of relatively equiaxed coarse grains. In contrast to our expectation, this effect of Cr addition is ascribable not to the pinning effect of $\delta$ phase due to Cr segregation but to the pinning effect of liquid phase due to the P segregation enhanced by the Cr addition. The important findings are summarized as follows.

1. In the samples with and without Cr addition cooled to room temperature, the as-cast $\gamma$ structure consists of Coarse Columnar $\gamma$ Grains (CCGs). The addition of 3 mass% Cr reduces the major axis diameter of the CCGs, resulting in the decrease in aspect ratio from 4.6 to 2.0.

2. During solidification process, the Fine Columnar $\gamma$ Grains (FCGs) forms at the front of the CCG region in the samples with and without Cr addition. The migration velocity of the FCG/CCG boundary was reduced by the Cr addition.

3. The Cr addition lowers the temperature for completion of $\gamma$ transformation, $T_\gamma$, by enhancing high P segregation. Then, the lowering of $T_\gamma$ reduces the migration velocity of the FCG/CCG boundary and relatively large grains grow into coarse grains in the FCG region in the sample with 3 mass% Cr, which results in the formation of the CCGs having shorter major axis diameters.

Acknowledgment

This work is partly supported by 18th ISIJ Research Promotion Grant.

REFERENCES