Grain-growth-inhibiting Effects of TiC and ZrC Precipitates in Fe–0.15–0.30mass% C Alloy

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The crystallization and precipitation of TiC and ZrC in an Fe–0.05–0.30mass% C alloy have been studied from the measurement of particles located at interdendritic region and austenite grain boundaries. The particles and γ grains were observed with the samples quenched at 1 673–1 743 K and those for holding at 1 673 K for 0–180 min. In an Fe–0.05–0.30mass% C–0.03mass% Ti alloy with soluble oxygen, the precipitation of Ti(O, C) occurs at 0.15 and 0.30 mass% C, while it does not at 0.05 mass% C. The cross section area of particles increases with increasing carbon contents. In the case of TiC precipitation in an Fe–0.20mass% C–0.06–0.22mass% Ti alloy the particles at interdendritic region dissolve and re-precipitate at γ grain boundaries during holding at 1 673 K for 0–120 min. The TiC particles at γ boundaries dissolve after 60 min, whereby resulting in the abnormal grain growth. In the case of ZrC precipitation in an Fe–0.20mass% C–0.02–0.27mass% Zr alloy, however, the ZrC particles at interdendritic region dissolve and continuously re-precipitate at γ grain boundaries up to 180 min, whereby resulting in the normal grain growth.

KEY WORDS: crystallization; precipitation; TiC; ZrC; solute micro segregation; austenite grain growth; abnormal grain growth.

1. Introduction

The influence of the precipitation and dissolution of carbide and nitride particles on austenite grain growth has been studied during heat treatment of as-cast sample by many researchers. However, there are few reports dealing with the effect of carbide particles on the austenite grain growth at non-steady state in the samples cooled from a melt. It has been known that the carbide former such as Ti or Zr easily segregates to the interdendritic region, whereby resulting in the crystallization and precipitation of carbide. These particles which are in non-equilibrium state start to dissolve by the solute homogenization during heat treatment. With increasing holding time or decreasing temperature, the re-precipitation of carbide occurs in the interior of dendrite arm, namely, the interior of the solute micro segregation domain.

The degree of solute segregation increases with increasing cooling rate at a constant cell dimension. However, since the cell dimension decreases with increasing cooling rate, the solute concentration profile in segregation domain after solidification is almost independent of cooling rate. It is to be noted that when the solute segregation occurs at high cooling rate, the rate of solute homogenization becomes high due to the decrease in cell dimension. In addition to this solute homogenization in segregation domain, the solute segregates to the austenite grain boundaries and this mechanism is supposed to be due to the non-equilibrium grain boundary segregation. Consequently, the solute segregated at austenite grain boundaries starts to precipitate at grain boundaries, thus leading to the effective pinning of initial γ grain growth. These grain boundary precipitates, which are in non-equilibrium state, dissolve and re-precipitate intragranularly during the period of holding and cooling.

In single phase solidification of an Fe–C(>0.51mass%) alloy where the solidification structure is equal to the initial austenite grain, the TiC or ZrC particles, which crystallize and precipitate at interdendritic region, can effectively inhibit the initial austenite grain growth. In the two-phase solidification of an Fe–C(<0.51mass%), however, solidification structure is not simply related to the initial austenite grains and the relation between the two depends on the solidification mode. Therefore, the effect of these precipitates on austenite grain growth is strongly dependent on the behavior of dissolution and precipitation of TiC or ZrC particles at interdendritic region and austenite grain boundaries.

Soluble oxygen content after Ti deoxidation is relatively high compared with Zr deoxidation. Thus, even in the presence of high carbon, the Ti(O, C) particles can crystallize and precipitate at interdendritic region as a result of solute micro segregation. In this study, an Fe–0.05–0.30mass% C–1.0mass% Mn–1.0mass% Ni alloy is deoxidized with Ti (0.03mass%) at 1 873 K, followed by cooling to a given temperature to
study the effect of Ti(O, C)$_x$ particles on austenite grain-growth-inhibition. On the basis of these results, the crystallization and precipitation of TiC and ZrC particles have been studied in the experiments where an Fe–0.20%C–0.02%P–Ti(Zr) alloy with a negligibly small amount of soluble oxygen is cooled to 1 673 K and held for 0 to 180 min, followed by quenching. The effect of these crystallized and precipitated particles of TiC and ZrC on austenite grain growth has been studied.

2. Experimental

The experimental procedures are explained as follows. Note that the Ti(O, C)$_x$ formation in liquid and solid states denote the crystallization and precipitation by definition, respectively. However, if it is not certain we use the precipitation.

2.1. Ti(O, C)$_x$

An Fe–0.05(0.15 and 0.30)%C–1.0%Mn–1.0%Ni alloy (70 g) was melted at 1 873 K in an Al$_2$O$_3$ crucible using an induction furnace and an Fe–10%Ti alloy (0.03%) was added to a melt containing an initial oxygen content of 80 to 120 ppm (% and ppm represent mass% and mass ppm, hereinafter). The melt was cooled to 1 673 (0.05% C), 1 743 (0.15% C) and 1 733 K (0.30% C) with a cooling rate of 50 K·min$^{-1}$, followed by quenching in water. These quenching temperatures determined by cooling curves correspond to the start temperature of the γ single phase. More details are given elsewhere. The methods for the measurement of inclusion characteristics and austenite grain size are given elsewhere along with those for the chemical analysis. The solidification microstructure was detected by the Ni concentration map which was obtained from Ni-Kα characteristic X-ray intensities. The composition of Ti(O, C)$_x$ particles precipitated during solidification was determined by the X-ray intensities of Ti, O and C in an Fe–0.05–0.30%C–1.0%Mn–1.0%Ni–0.03%Ti alloy with soluble oxygen which was cooled to 1 473 K, followed by water quenching.

2.2. TiC and ZrC

An Fe–0.20%C–0.02%P alloy (70 g) was melted at 1 873 K in an Al$_2$O$_3$ crucible for TiC and a MgO or ZrO$_2$ crucible for ZrC under an Ar–7%H$_2$ atmosphere using an induction furnace and then an Fe–10%Zr or Fe–10%Ti alloy was added. The melt was cooled to 1 673 K with a cooling rate of 50 K·min$^{-1}$ and held for 0–180 min, followed by quenching in water. The size and number of precipitates were measured by SEM and optical microscope. The carbide precipitates were identified by XRD and EPMA-WDX. Austenite grain boundaries were revealed after etching by 10% nital solution. The ratio of particles at grain boundaries to total number of particles per unit area, $\Phi_{A_T}$, was obtained by the method described in detail elsewhere. Solidification structure was observed after etching by the method given elsewhere.

3. Results and Discussion

3.1. Effect of Ti(O, C)$_x$ Precipitates on γ Grain Size

3.1.1. Precipitation Behavior

The effect of deoxidation product with Ti on γ grain size has been studied. It was found that the grain-growth-inhibition by titanium oxide is smaller compared with that of other oxides such as MgO, Ce$_2$O$_3$ and ZrO$_2$ due to smaller number of titanium oxide particles. There are very few reports dealing with the effect of secondary titanium oxide particles precipitated during solidification on grain-growth-inhibition. It has been well established based on the solute micro segregation model that the amount of particles crystallized and precipitated during solidification is strongly affected by carbon content, which may determine the solidification mode at a given solidification condition. It is expected that the amount of Ti(O, C)$_x$ crystallized during solidification at 0.05% C is much smaller than that at 0.15 and 0.30% leading to a smaller degree of solute segregation.

The solidification structure is shown in Fig. 1(a) in which the area specified is magnified in Fig. 1(b). The dark area corresponds to a primary dendrite arm. If the grain growth of initial primary dendrite arm is completely suppressed by particle pinning, it is expected that the thin lines observed in Fig. 1(b) correspond to the initial austenite grain boundaries or not. The Ti-Kα X-ray image is shown in Fig. 1(c) which shows higher magnification of the marked area in Fig. 1(d). Figure 1(d) shows the Ni-Kα X-ray intensity map of the same area as Fig. 1(b). It is realized that precipitates are significantly concentrated at the interdendritic region where Ni content is high, particularly at triple point.

The composition of the substance consisting of Ti was determined by EDX analysis. The component images of Ti, C and O X-ray intensity maps have proved that the substance is identified as Ti(O, C)$_x$ and the ratio of TiC to Ti$_2$O$_3$ in mass% is 3.3 to 3.5. The size of a particle precipitated in chain is about 1 μm. These precipitated particles were observed at 0.15 and 0.30% C quenched at different quenching temperatures, while not at 0.05% C.

The comparison between initial γ grain boundaries and solidification structure of dendrites was made for the samples at 0.15 and 0.30% C which were cooled to 1 743 and 1 733 K, respectively, followed by quenching in water. These temperatures are the γ start temperatures. In the case of 0.50% C with the single phase solidification of γ phase, it was found that the initial γ grain corresponds to a primary dendrite arm. If the grain growth of initial γ is completely suppressed by particle pinning, it is expected that γ grain should be originated from each dendrite. In the cases of 0.15 and 0.30% C, however, the initial γ grain boundaries which are completely pinned do not coincide with the solidification structure. This is because the place of γ phase nucleated at δ/liquid interface depends on solidification mode and solidification parameters.

As shown in Fig. 1, the Ti(O, C)$_x$ particles are located at the interdendritic region which coincides with the initial δ grain boundaries. By using the method described previously, the solidification structure with primary dendrite arms was superimposed with the microstructure with γ grain boundaries in the same area observed in the solidification structure. It was found that precipitated particles are
located at some of $\gamma$ grain boundaries which agree to the final solidification surface. But no particles are located at $\gamma$ grain boundaries which do not coincide with the final solidification surface.

During cooling from the highest temperatures in single $\gamma$ phase region (1 673 K for 0.05% C, 1 743 K for 0.15% C and 1 733 K for 0.30% C) to 1 473 K, the $\gamma$ grain growth occurs; namely, the Ti(O, C) particles grow by coarsening and may coalesce if particles dragging occurs. The Ti(O, C) particles precipitated at interdendritic region dissolve and re-precipitate at $\gamma$ grain boundaries, as discussed in Sec. 3.3. The dissolution and precipitation behavior of Ti(O, C) particles which are non-equilibrium phase is complicated and influenced by initial solute contents, solidification parameters and the growth rate of $\gamma$ grains.

3.1.2. Carbon Content

In this section the $\gamma$ grain size pinned by the Ti(O, C) particles is discussed as a function of carbon content, that is, solidification mode. Chemical compositions of total O and soluble and insoluble deoxidant (M), and particle and $\gamma$ grain characteristics are summarized in Table 1, in which Exp. 1, 2, 4 and 9 have been already carried out in the previous study.3)

![Fig. 1. Solidification structure (a), $\gamma$ grain (b), Ti-K (c) and Ni-K (d) in Fe–0.15%C–1.0%Mn–1.0%Ni–0.03%Ti alloy.](image)

![Table 1. Chemical compositions of total O and soluble and insoluble M, and particle and grain characteristics in Fe–0.05~0.30%C–1.0%Mn–1.0%Ni alloy.](table)

<table>
<thead>
<tr>
<th>Exp. No</th>
<th>Deoxidant</th>
<th>Temp. in water quenching (K)</th>
<th>$\bar{D}_x$ (mm)</th>
<th>$\bar{d}_x$ (mm)</th>
<th>$N_x$</th>
<th>$f_x$ (x10$^{-4}$)</th>
<th>T.C (%)</th>
<th>T.O (ppm)</th>
<th>Sol. M (ppm)</th>
<th>Insol. M (ppm)</th>
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<td>1.47</td>
<td>165</td>
<td>0.22</td>
<td>0.05</td>
<td>9</td>
<td>191</td>
<td>9</td>
</tr>
<tr>
<td>2</td>
<td>Ti</td>
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<td>1.44</td>
<td>0.99</td>
<td>237</td>
<td>1.02</td>
<td>0.05</td>
<td>8</td>
<td>240</td>
<td>4</td>
</tr>
<tr>
<td>3</td>
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<tr>
<td>4</td>
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<td>1473</td>
<td>1.01</td>
<td>0.97</td>
<td>319</td>
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<td>0.15</td>
<td>15</td>
<td>295</td>
<td>8</td>
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<td>1743</td>
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<td>0.15</td>
<td>6</td>
<td>163</td>
<td>33</td>
</tr>
<tr>
<td>7</td>
<td>Ti</td>
<td>1673</td>
<td>0.46</td>
<td>0.77</td>
<td>103</td>
<td>0.30</td>
<td>0.20</td>
<td>23</td>
<td>254</td>
<td>12</td>
</tr>
<tr>
<td>8</td>
<td>Ti</td>
<td>1473</td>
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<td>1.18</td>
<td>41</td>
<td>1.02</td>
<td>0.30</td>
<td>50</td>
<td>162</td>
<td>40</td>
</tr>
<tr>
<td>9</td>
<td>Ti</td>
<td>1733</td>
<td>0.58</td>
<td>0.97</td>
<td>268</td>
<td>1.22</td>
<td>0.30</td>
<td>7</td>
<td>226</td>
<td>48</td>
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$\bar{D}_x$: $\gamma$ grain diameter, $\bar{d}_x$: particle diameter (2D), $N_x$: number of particles per unit area, $f_x$: volume fraction of particles.
The mean austenite grain diameter, $\bar{D}_A$, obtained by quenching at respective temperatures and that obtained at 1473 K are plotted against quenching temperatures in the upper diagram of Fig. 2. It can be seen that the $\bar{D}_A$ values for 0.05 and 0.30% C are almost independent of quenching temperature, indicating that there is no $\gamma$ grain growth during cooling. In the case of 0.05% C in which no segregation of solutes of Ti and O occurs due to a higher solute diffusion rate in $\delta$ phase, no precipitation of Ti(O, C)$_x$ particles was observed. Because the inhibition of grain growth by pinning did not occur, it is considered that the observed $\bar{D}_A$ values are almost at steady state.

The $\bar{D}_A$ values are plotted against carbon content in the lower diagram of Fig. 2. It is clear that the $\bar{D}_A$ values below 0.10% C are higher than those over 0.10% C. In order to explain these results, the number and size of precipitates was measured. However, since Ti(O, C)$_x$ particles precipitate in chain, the cross section area of Ti(O, C)$_x$ particles per unit area was measured.

The relationship between cross section area of Ti(O, C)$_x$ particles and carbon content is shown in the upper diagram of Fig. 3. The $\bar{D}_A$ vs. cross section area of Ti(O, C)$_x$ particles is shown in the lower diagram of Fig. 3. The amount of Ti(O, C)$_x$ particles increases with an increase in carbon content over 0.1% below which no particles were observed, whereby leading to the decrease in the $\bar{D}_A$ value. The results shown in the lower diagram of Fig. 2 are well supported by this tendency. The higher $\bar{D}_A$ values below 0.10% C is attributed to the fact that $\gamma$ grain growth occurs extensively during cooling at initial stage, thus approaching to the steady state value. The growth rate can be estimated from the slope in the upper diagram of Fig. 2, since the time during cooling is obtained by cooling rate. The lower growth rate for 0.30% C than for 0.15% C is due to the less amount of pinning particles shown in the upper diagram of Fig. 3, showing the amount of Ti(O, C)$_x$ particles at 0.30% C is larger than that at 0.15% C.

In order to study the effect of only TiC on the $\gamma$ grain size, an Fe–0.15%C–1.0%Mn–1.0%Ni–0.03%Ti alloy was deoxidized with Al at 1873 K and held for 30 min to remove Al$_2$O$_3$ particles by flotation. Then, an Fe–10%Ti alloy (initial Ti content of 0.03%) was added to the melt that was then cooled to 1743 K, followed by water quenching. The datum point for TiC particles given in Table 1 is shown in the lower diagram by an asterisk (*). It was observed that Ti(O, C)$_x$ particles are located at interdendritic region at initial stage, indicating that precipitation occurs due to the solute micro segregation. With the growth of $\gamma$ grain, however, they are located at $\gamma$ grain boundaries which coincide with the interdendritic regions. These results suggest that Ti(O, C)$_x$ particles which precipitate in non-equilibrium state dissolve and re-precipitate at $\gamma$ grain boundaries. In order to clarify this phenomena, the experiments described in Sec. 2.2 have been carried out.

3.2. Effect of Precipitation Behavior of TiC and ZrC on $\gamma$ Grain Size

3.2.1. Precipitation Behavior

The experimental conditions, particle characteristics and metal compositions are summarized in Table 2.

In the case of TiC precipitation shown in the upper diagram of Fig. 4, the precipitated amount of TiC remains constant when [T.Ti]/H$_{11005}$=0.09–0.10%, but that decreases considerably when [T.Ti]=0.19–0.21% after 60 min. These results imply that the TiC precipitates dissolve when [T.Ti]=0.2%. The content of ZrC precipitation shown in
On the other hand, the precipitation rate is more enhanced at higher total Zr content. Zirconia carbide particles were observed at grain boundaries, while TiC particles completely disappear after holding for 180 min. This contrary behavior cannot be explained simply by the difference in equilibrium constants of TiC (Ti\(_{g}/\text{H}_{11001}\)C: K\(_{\text{TiC}}/\text{H}_{11005}/\text{H}_{11002}\) 1.43 at 1673 K) and ZrC (Zr\(_{g}/\text{H}_{11001}\)C: K\(_{\text{ZrC}}/\text{H}_{11005}/\text{H}_{11002}\) 1.22 at 1673 K). It depends on the parameters affecting the nucleation and growth of carbide, those affecting the grain size and those affecting non-equilibrium grain boundary segregation.1,2)

In this study the area fraction of particles per unit area, \(S_A\), the mean size of particles, \(d_A\), and the number of particles per unit area, \(N_A\), are measured on cross section. The mean particle size calculated from the measured \(S_A\) and \(N_A\) values, \(d_A^{\text{cal}}\), assuming that a particle has the diameter of a circle with the same area of a sectioned particle is expressed as follows:

\[
d_A^{\text{cal}} = (4S_A)^{1/2}/(\piN_A)^{1/2}
\]

The particle area fraction, \(S_A^{\text{cal}}\) was calculated from the same assumption mentioned above as follows:

\[
S_A^{\text{cal}} = (\pi/4)d_A^{\text{cal}}N_A
\]

The measured \(S_A\), \(N_A\) and \(d_A\) values in conjunction with the calculated \(S_A^{\text{cal}}\) values from Eq. (2) and \(d_A^{\text{cal}}\) values from Eq. (1) are plotted against holding time in Fig. 5. The values obtained by quenching immediately after solidification (1743 K) are shown by the diamond marks. The experiment for 120 min when [T.Ti]/\(\text{H}_{11002}\) 0.1% was not made. The \(S_A\) values (the amount of TiC precipitates) decrease continuously indicating the dissolution of TiC particles. In the case of \([\text{T.Ti}/\text{H}_{11002}] 0.2\%\), the \(N_A\) values increase and the \(d_A\) values decrease under the decrease in the \(S_A\) value. These results indicate that total amount of precipitates decreases, but number of small particles increases. The increase in \(N_A\) and the decrease in \(d_A\) can be explained by the re-precipitation of TiC particles at grain boundaries. In the case of \([\text{T.Ti}/\text{H}_{11002}] 0.09\%/\text{H}_{11011}\ 0.12\%\), the TiC particles tend to slightly precipitate until 60 min and then start to dissolve. The precipitated TiC particles at interdendritic region in non-equilibrium state approach to the equilibrium state by solute homogenization. It is evident that the solute contents at interdendritic region is higher than that in the interior of dendrite arm which corresponds to the intragranular region of initial \(\delta\) grain.

The precipitation behavior for ZrC is shown in Fig. 6.

**Table 2.** Experimental conditions, particle characteristics and metal compositions in Fe–0.20%C–0.02%P–Ti(Zr) alloy.

<table>
<thead>
<tr>
<th>Exp.No</th>
<th>Holding time at 1673K (min)</th>
<th>(S_A)</th>
<th>(d_A)</th>
<th>(N_A)</th>
<th>(\Phi^\text{A})</th>
<th>(D_{\text{mean}})</th>
<th>(D_{\text{mean}}/D_{\text{mean}})</th>
<th>(\alpha / D_{\text{mean}})</th>
<th>T.C.</th>
<th>T.O.</th>
<th>T.M.</th>
<th>T.A(Mg)</th>
<th>Insol. M</th>
<th>Insol. Al(Mg)</th>
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<tr>
<td>T5</td>
<td>0</td>
<td>7.3</td>
<td>2.1</td>
<td>222</td>
<td>0.68</td>
<td>400</td>
<td>2.3</td>
<td>0.27</td>
<td>200</td>
<td>16</td>
<td>1029</td>
<td>81</td>
<td>172</td>
<td>43</td>
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<tr>
<td>T7</td>
<td>60</td>
<td>8.0</td>
<td>1.7</td>
<td>379</td>
<td>0.64</td>
<td>655</td>
<td>4.6</td>
<td>0.73</td>
<td>202</td>
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<td>863</td>
<td>66</td>
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<td>49</td>
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<tr>
<td>T8*</td>
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<td>12.4</td>
<td>2.8</td>
<td>213</td>
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<td>384</td>
<td>2.3</td>
<td>0.29</td>
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<td>129</td>
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<td>T9*</td>
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<td>11.5</td>
<td>2.3</td>
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<td>500</td>
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<td>355</td>
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<tr>
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<tr>
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<td>1040</td>
<td>0.02</td>
<td>588</td>
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</table>

* Al deoxidation ** quenched at 1773K A: abnormal growth area n.a.: not analyzed
The increase in the $S_A$ values indicates the continuous precipitation of ZrC particles until 60 min. Differing from TiC, the $S_A$ values decrease slightly after 60 min and the $N_A$ and $d_A$ values tend to decrease slightly except for $[T.Zr]/H11005=0.15$--$0.28\%$. The increase of $N_A$ and the decrease of $S_A$ after 60 min observed when $[T.Zr]/H11005=0.15$--$0.28\%$ suggest that the ZrC particles located at interdendritic region dissolve and re-precipitate at $\gamma$ grain boundaries. The difference in the precipitation behavior between TiC and ZrC particles can be summarized as follows; the ZrC particles when $[T.Zr]/H11005=0.19\%$ re-precipitate continuously at $\gamma$ grain boundaries after dissolution of particles precipitated at interdendritic region. On the other hand, the TiC particles when $[T.Ti]/H11005=0.09$--$0.21\%$ precipitated at interdendritic region dissolve and re-precipitate at $\gamma$ grain boundaries, but they start to dissolve after 60 min.

The precipitation behavior of TiC and ZrC in solidification micro segregation domain has been studied for the sample quenched at 0 min holding time at 1 673 K. The $S_A$, $N_A$ and $d_A$ values measured as a function of area fraction of solid, $f_S$, described elsewhere$^{13)}$ for TiC and ZrC are shown in Figs. 7 and 8, respectively. In Fig. 7 the $S_A$ and $N_A$ values when $[T.Ti]=0.19\%$ are even higher at interdendritic region which corresponds to higher $f_S$ than for $[T.Ti]=0.08$ and $0.12\%$. These results suggest that at $[T.Ti]=0.19\%$, the TiC particles precipitate at interdendritic region at the final stage of solidification. In Fig. 8, the $S_A$ and $N_A$ values for ZrC precipitation in-

Fig. 5. Variation of $S_A$, $N_A$ and $d_A$ values for TiC precipitates with holding time at 1 673 K.

Fig. 6. Variation of $S_A$, $N_A$ and $d_A$ values for ZrC precipitates with holding time at 1 673 K.

Fig. 7. Precipitation behavior of TiC in solidification segregation domain for 0 min holding time at 1 673 K.

Fig. 8. Precipitation behavior of ZrC in solidification segregation domain for 0 min holding time at 1 673 K.
increase gradually with an increase in $f_g$. This behavior is different from that of TiC. This implies that under the present experimental condition ZrC particles are dispersed more uniformly in segregation domain in comparison with the case of TiC particles.

An Fe–0.20%C–0.02%P–0.10%Ti alloy was cooled to 1673 K or 1273 K at 50 K·min$^{-1}$, followed by rapid quenching. The $S_A$, $N_A$ and $d_A$ values are measured as a function of $f_g$, as shown in Fig. 9. The $S_A$ and $N_A$ values for 1673 K are higher than those for 1273 K. These results suggest that TiC particles precipitated as a result of solute segregation dissolve during cooling. However, it is not certain if dissolved TiC particles re-precipitate at grain boundaries.

3.2.2. Grain-growth-inhibition

In order to confirm the re-precipitation of TiC at γ grain boundaries, the following analysis has been made.

The fraction of particles at γ grain boundaries to total particles is defined by Eq. (3)

$$\Phi^N_A = n^{GB}/n$$

where $n^{GB}$ is the number of particles at grain boundaries per unit area and $n$ is the total number of particles per unit area.

If the particles are dispersed randomly, the fraction of particles at γ grain boundaries to total particles per unit area is expressed as follow$^{41}$:

$$\Phi^{R}_A = 2d_A/\bar{D}_A$$

The calculated fraction of particles at grain boundaries, $\Phi^{cal}_A$, is defined as

$$\Phi^{cal}_A = n^{GB(=0.8-1.0)}/n$$

where $n^{GB(=0.8-1.0)}$ is the particles located when $f_g=0.8-1.0$ per unit area which can be measured from a plot of $N_A$ vs. $f_g$.

The $\Phi^N_A$, $\Phi^R_A$ and $\Phi^{cal}_A$ values, which represent the fraction of randomly dispersed particles at γ grain boundaries, for TiN precipitates are plotted against holding time at 1673 K in Fig. 10. The decrease in $\Phi^N_A$ value is due to not only particle dissolution at γ grain boundaries, but also to the γ grain growth. The $\Phi^{R}_A (=2d_A/\bar{D}_A)$ values tend to decrease with holding time, indicating that γ grain size increases. Therefore, the $\Phi^{R}_A/\Phi^{R}_A$ ratios are plotted against holding time at 1673 K as well. It can be seen that these ratios increase up to 60 min and thereafter decrease. These results indicate that the particles located at interdendritic region first dissolve and small particles precipitate at γ grain boundaries up to 60 min. The particles at γ grain boundaries dissolve after 60 min.

Figure 11 shows the results for ZrC precipitates. The $\Phi^N_A$ values decrease gradually, as is observed in TiC precipitates as a result of γ grain growth. The $\Phi^R_A$ and $\Phi^{R}_A/\Phi^{R}_A$ values increase gradually or tend to be saturated. These behaviors are different from those observed in TiC precipitates in that these values decrease after 60 min. These results indicate that the ZrC particles precipitated at interdendritic region dissolve first and re-precipitate continuously at γ grain boundaries up to 180 min. In the case of [Ti]Zr$=0.02-0.03\%$, the ZrC particles precipitated at γ grain boundaries start to dissolve after 60 min.

The mean γ grain size, $D_{mean}$, the ratio of maximum γ grain, $D_{max}$, to $D_{mean}$, and the ratio of the standard deviation of grain size distribution, $\sigma$, to $D_{mean}$ are plotted against the holding time at 1673 K in Figs. 12 and 13 as functions of Ti and Zr contents, respectively. The physical meaning of $D_{max}/D_{mean}$ and $\sigma/D_{mean}$ are the degree of abnormal growth and how widely the grain size scatters, respectively. One can understand in Fig. 12 that the γ grain size distributions change from normal to abnormal growth with an increase in holding time from 0 to 60 min and then approach normal growth after 60 min. This behavior can be explained by the behavior of TiC particles shown in Figs. 5 and 10. It is seen
from Fig. 5 that the TiC particles dissolve continuously and from Fig. 10 that the particles re-precipitate at γ grain boundaries from 0 to 60 min and then the precipitates at grain boundaries dissolve.

It is seen from Fig. 13 that the behavior of γ grain size and dissolution of ZrC particles is completely different from that for TiC particles. Every value tends to increase from 0 to 60 min and remains almost constant after 60 min. The $D_{\text{max}}/D_{\text{mean}}$ tendency proves that the normal grain growth has taken place. These results can be supported by the fact that ZrC particles tend to increase from 0 to 60 min and then gradually decrease, as shown in Fig. 6. Furthermore, the ZrC particles at interdendritic region dissolve and continuously precipitate at γ grain boundaries from 0 to 180 min except for the results of 0.02% Zr, as is obvious in Fig. 11.

The precipitation behaviors of TiC and ZrC particles are schematically illustrated in Fig. 14. The ZrC particles at interdendritic region disperse more widely, whereas the TiC particles locate only at the final solidification place. The
precipitated amount of TiC particles is smaller than that of ZrC particles, and the size of the former is nearly the same as that of the latter. After particle dissolution, the re-precipitation at γ grain boundaries occurs. The precipitated amount of ZrC particles is larger than that of TiC particles. The number ratio of ZrC particles at γ grain boundaries to total number of particles per unit area, compared with that for random particle distribution, $\Phi_N^g/\Phi_R^g$, is larger than that of TiC particles. Furthermore, this value for ZrC particles increases continuously, while that for TiC particles decreases due to particle dissolution after 60 min. Consequently, the abnormal growth is observed for TiC particles.

4. Conclusions

The behavior of crystallization and precipitation of TiC and ZrC in an Fe–0.05–0.30%C alloy has been studied from the measurement of particle dispersion with respect to interdendritic region and γ grain boundaries during holding at 1 673 K. The behavior of the inhibition of austenite grain growth by these particles has been studied. The following conclusions are drawn:

(1) The cross section area of Ti(O, C)$_x$ particles in an Fe–0.05–0.30%C–0.03%Ti alloy increases with carbon content above 0.1% C, while no precipitation of Ti(O, C)$_x$ at 0.05% C. The γ grain size decreases with an increase in cross section area of Ti(O, C)$_x$ particles.

(2) The TiC particles precipitated at interdendritic region dissolve and re-precipitate at γ grain boundaries in an Fe–0.20%C–0.06%Ti alloy during holding at 1 673 K for 120 min. The TiC particles at γ grain boundaries dissolve and thus abnormal grain growth occurs.

(3) The ZrC particles precipitated at interdendritic region dissolve and re-precipitate at γ grain boundaries in an Fe–0.20%C–0.02,0.27%Zr alloy during holding at 1 673 K for 60 min. The ZrC precipitation at γ grain boundaries continuously occurs from 60 to 180 min, and thus the normal grain growth occurs.

REFERENCES