Effect of Annealing Before Cold Forging on the Behavior of Abnormal Grain Growth during Carburizing

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In order to clarify the mechanism of abnormal grain growth in steel for cold forging and carburizing, the effect of spheroidizing annealing on the behavior of abnormal grain growth during carburizing was investigated. Abnormal grain growth was observed in annealed steel, whereas it was suppressed in normalized steel. However, since both the normalized steel and the annealed steel have almost the same size distribution of Nb(C,N) nano-precipitates, the effect of annealing on abnormal grain growth was not explained by the conventional theory based on the pinning force by nano-precipitates.

Spheroidized cementite was remained in the annealed steel which was immediately quenched from the quasi-carburizing temperature of 1,203 K. Dissolution of spheroidized cementite and abnormal grain growth took place simultaneously. Spheroidized cementite was thermally stabilized by Cr concentration. A DICTRA simulation was carried out to discuss the kinetics of cementite dissolution. Cr concentration affects the dissolution rate of spheroidized cementite through the relationship between the Cr content and the cementite size. The Cr content in cementite has a wide distribution, and the dissolution time is different in each cementite. This dissolution time lag among cementites causes a local and non-uniform decrease of the pinning force by cementite. As a consequence, abnormal grain growth is likely to occur in annealed steel.

KEY WORDS: grain growth; carburizing; annealing; cold forging; pinning; spheroidized cementite.

1. Introduction

Carburizing, quenching and tempering treatment (hereinafter referred to as “carburizing”) is a heat treatment process which is effective for improving fatigue characteristics, even among general-purpose surface hardening heat treatments. However, because it involves long-term heating in the austenite (hereinafter referred to as γ region, abnormal grain growth of γ (secondary recrystallization) may occur. It is important to prevent abnormal grain growth of γ as it is both a factor in lowering fatigue characteristics and a factor in increasing heat treatment strain. Gladman proposed a critical condition formula for abnormal grain growth based on the relationship between the driving force of grain growth and the pinning force exerted by precipitate particles. According to that theory, as the volume fraction of precipitate particles increases or the precipitate particles become finer, the pinning force increases and abnormal grain growth is suppressed. On the other hand, as the grain size becomes finer, the driving force of grain growth increases, and abnormal grain growth tends to occur. Thus, it is possible to prevent abnormal grain growth by controlling the precipitate particles and the γ grain distribution. The most common way to prevent abnormal grain growth is to utilize the pinning effect on the γ grain boundary exerted by fine precipitate particles such as Nb(C,N).

In addition to the steel composition, forging conditions also greatly influence the distribution of precipitate particles and γ grains. According to Fujimatsu et al., abnormal grain growth tends to occur in a region where the shear strain introduced by cold forging is high (hereinafter referred to as macro shear band). The reason for this is considered to be that the γ grains are refined by refinement of recrystallized ferrite (hereinafter referred to as α). In the experimental results of Kubota and Ochi when spheroidizing annealing is performed in the α/γ two-phase region before cold forging, the temperature for generation of coarse grains drops. This is presumed to occur because extended heating during spheroidizing annealing causes coarsening of precipitate particles, and as a result, their pinning force decreases. On the other hand, according to Tominaga et al., spheroidizing annealing before cold forging does not significantly affect the dispersion state of precipitate particles, but abnormal grain growth is likely to occur through γ grain refinement in the initial stage of carburizing. As described above, numerous studies have investigated abnormal grain growth during carburizing, but prevention of abnormal grain growth is still considered to be an important task for manufacturing actual parts and has not been solved. Therefore, in this study, the process of microstructural change during carburizing was observed in...
detail, focusing on the cold forging process, which is said to cause abnormal grain growth easily, and the mechanism of occurrence of abnormal grain growth was discussed.

2. Experimental Procedure

2.1. Sample Material

Table 1 shows the chemical compositions of the test material. Steel, in which 0.024%Nb was added to the base chemical compositions of SCM420, was melted in a 150 kg steel ingot by vacuum induction melting. After heating to 1 493 K, the ingot was forged into a round bar having a diameter of 45 mm, which was subjected to heat treatment under the conditions of holding at 1 173 K for 3.6 ks followed by air cooling (hereinafter referred to as “Normalized steel”). In order to investigate the effect of spheroidizing annealing before cold forging on abnormal grain growth behavior during carburizing, spheroidizing annealing was applied to the Normalized steel. Figure 1 shows the spheroidizing annealing pattern, which comprised cooling at 0.004 K/s after holding at 1 033 K for 28.8 ks. Hereinafter, the steel subjected to spheroidizing annealing is referred to as “Annealed steel.”

2.2. Cold Forging and Heat Treatment Conditions

Cold forging was conducted in accordance with cold upset compression test method established by the Cold Forging Subcommittee of the Japan Society for Technology of Plasticity. Cylindrical specimens with a diameter of 15 mm and a height of 22.5 mm were taken from the Normalized steel and the Annealed steel by cutting. Cold upsetting compression was applied to the cylindrical specimens to a height reduction rate of 70% by using a die with concentric grooves. In order to investigate the abnormal grain growth behavior during carburizing, the specimens after cold upsetting compression were subjected to the quasi-carburizing heat treatments shown in Fig. 2. As shown in the figure, after heating to 1 203 K at 0.26 K/s, the specimens were quenched immediately or quenched after holding for various times. Here, quasi-carburizing refers to a process simulating only the thermal history of carburizing in a nitrogen atmosphere, not in a carburizing gas atmosphere.

2.3. Microstructure Observation and Analysis Method

In order to confirm the initial microstructure before quasi-carburizing, the Normalized steel and the Annealed steel before and after cold forging were observed with an optical microscope. The specimens were prepared by mirror polishing followed by 3% nital etching. Observation of prior γ grains after quasi-carburizing was carried out using specimens etched with a picric acid aqueous solution after mirror polishing. Benzene sulfonic acid was added to the picric acid aqueous solution to promote the appearance of the prior γ boundary.

A scanning electron microscope (hereinafter referred to as SEM) was used to investigate the microstructural change during quasi-carburizing in detail. The alloy content distribution in the microstructure was measured with an energy dispersive X-ray spectroscope (hereinafter referred to as SEM-EDX) mounted in the SEM.

Precipitate particles were observed by the extraction replica method by using a transmission electron microscope (hereinafter referred to as TEM). The precipitate particles were identified with an energy dispersive X-ray spectroscope (TEM-EDX) mounted in the TEM.

The observation positions after cold forging and after quasi-carburizing were unified to the macro shear band position18,24,25 where abnormal grain growth is likely to occur, as shown in Fig. 3, in both the optical microscope observation and the observation by TEM and SEM.

2.4. Quantitative Evaluation Method of Microstructure

In order to verify the theory proposed by Gladman, the prior γ grain radius and precipitate particle radius were quantitatively evaluated. For the prior γ grain radius, microstructural images taken with an optical microscope were analyzed by image analysis to obtain a total of two hundred γ grain areas individually and evaluated as the mean prior γ grain radius. Similarly, the precipitate particle radius was measured from SEM images.

![Fig. 1. Spheroidizing annealing conditions.](image1)

![Fig. 2. Heat treatment conditions for quasi-carburizing.](image2)

![Fig. 3. Observation positions of electron and optical microscopes.](image3)
average equivalent circle radius. The image analysis software used was Image-Pro PLUS (manufactured by Media Cybernetics). TEM images were used for evaluation of the precipitate particle radius. For the precipitate particle radius, as in the case of the prior γ grain radius, a total of two hundred precipitate particle areas were individually calculated by image analysis and evaluated as the average equivalent circle radius.

In order to investigate the effect of spheroidized cementite on abnormal grain growth behavior, a total of one hundred cementites were analyzed from SEM images, and the circle equivalent radius was obtained.

3. Experimental Results

3.1. Microstructure Before and After Quasi-carburizing

Figure 4 shows optical microscope images of the Normalized steel and Annealed steel before and after cold forging. The Normalized steel before cold forging had a two-phase microstructure composed of α and pearlite (Fig. 4(a)). After cold forging, the α and pearlite phases exhibited a plastically deformed and elongated microstructure (Fig. 4(b)). On the other hand, the Annealed steel before cold forging had a microstructure with α as the matrix phase, in which spherical cementite was dispersed (Fig. 4(c)). Plastic deformation was introduced by cold forging and elongated α phase was observed (Fig. 4(d)).

Figure 5 shows the results of observation of the prior γ grains after quasi-carburizing of cold forged Normalized steel and Annealed steel. Abnormal grain growth was not observed in the Normalized steel at any holding time, but abnormal grain growth occurred when the Annealed steel was held for 10.8 ks or more (Figs. 5(g) 5(h)). From this result, it was confirmed that abnormal grain growth is more likely to occur in the Annealed steel than in the Normalized steel, and this tendency is consistent with the previous report. In both the Normalized steel and the Annealed steel, the prior γ grains which were immediately quenched were well ordered and had an average radius of about 3.1 μm in the Normalized steel and a similar radius (2.7 μm) in the annealed steel. Therefore, in the scope of this experiment, the effect of the γ grain size in the initial stage of carburizing on abnormal grain growth is small.

3.2. Distribution of Precipitate Particles in Quasi-carburizing Process

It is thought that the relationship between the driving force of grain growth and the pinning force of the grain boundary exerted by precipitate particles strongly affects the occurrence of abnormal grain growth. Figure 6 shows the results of TEM observation of precipitate particles in the quasi-carburizing process. Fine precipitate particles with a radius of 5 to 8 nm were uniformly dispersed in both the Normalized steel and the Annealed steel with all the holding times. TEM-EDX analysis of these fine precipitate particles identified the precipitate particles as Nb(C,N) in both the Normalized steel and the Annealed steel. In addition to fine Nb(C,N), AlN was also observed at a low frequency, but the particle radius was as large as 40 to 60 nm, and no difference was observed between the Normalized steel and the Annealed steel.

3.3. Microstructure of the Annealed Steel Right After Heating in Quasi-carburizing

Figure 7 shows higher magnification images of Figs. 5(a), 5(e), right after heating in quasi-carburizing. As shown in Fig. 7(b), numerous black spots dispersed in the microstructure were observed in the Annealed steel. Figure 8

![Fig. 4. Optical micrographs of steels. (a) Normalized steel before cold forging (b) Normalized steel after cold forging (c) Annealed steel before cold forging (d) Annealed steel after cold forging.](image)

![Fig. 5. Optical micrographs of steels immediately quenched from 1203 K and quenched after 3.6 ks, 10.8 ks and 21.6 ks.](image)
The black spots were spherical, and Cr concentration was observed. From this result, it is inferred that the black spots are spheroidized carbides which formed during spheroidizing annealing and the carbides remained without forming a solid solution after reaching the quasi-carburizing temperature of 1203 K. In the result of the Cr content analysis of the spherical carbide described later, since the maximum content of the Cr was 18%, the spherical carbide observed in this study is considered to be cementite instead of alloy carbide.26)

4. Discussion

4.1. Conventional Theory of Abnormal Grain Growth

Gladman proposed the following Eq. (1) as a critical condition formula for abnormal grain growth from the relationship between the driving force of grain growth and the pinning force exerted by precipitate particles. Here, \( r^* \) is the critical precipitate particle radius causing abnormal grain growth, \( R_0 \) is the average \( \gamma \) grain radius, \( f \) is the volume fraction of precipitate particles, and \( Z \) can be considered to be 1.7 in the two-dimensional system.27,28) According to this formula, abnormal grain growth is suppressed when precipitate particles having a finer radius than the critical precipitate particle radius \( r^* \) are dispersed.

\[
r^* = \frac{6R_0 f}{\pi} \left( \frac{3}{2} \frac{2}{Z} \right)^{1/3}
\] .......................... (1)

Since Gladman proposed the Eq. (1), the discussion in most studies on abnormal grain growth of \( \gamma \) during carburizing has been based on Eq. (1). In particular, there are many studies3–20) on fine nano-sized precipitate particles with sizes of several nm to several 10 nm, such as Nb(C,N) and TiC. Fine Nb(C,N) with a particle radius of 5 to 8 nm was also observed in this study, as shown in Fig. 6. Therefore, the effect of spheroidizing annealing before cold forging on abnormal grain growth was discussed based on Eq. (1).

Figure 9 shows the distribution of the Nb(C,N) precipitate particle radius in the quasi-carburizing process. The dotted lines in the figure show the average precipitate particle radius. Precipitate particles of both the Normalized steel and the Annealed steel show Ostwald ripening as the holding time increases. However, the Normalized steel and the Annealed steel have almost the same average precipitate particle radius, and the distributions of their precipitate particle radii are also equivalent. Therefore, the effect of spheroidizing annealing before cold forging on the Nb(C,N) precipitate particle size is extremely small.

Figures 10(a) 10(b) shows the calculation results of the critical precipitate particle radius \( r^* \) and the actually measured precipitate particle radius. Here, the volume fraction \( f \) was calculated by using the density of NbC30) and \( \gamma \) after determining the weight of the precipitates at 1203 K from the solubility product of NbC in \( \gamma \).29) After holding for 10.8 ks, the measured values of average precipitate particle radius \( r^* \) of both the Normalized steel and the Annealed steel was larger than the critical precipitate particle radius \( r^* \), and consequently the condition for occurrence of abnormal grain growth was satisfied. Besides Nb(C,N), AlN with a particle radius of 40–60 nm was also observed at low
frequency as precipitate particles in both the Normalized steel and the Annealed steel. Similarly to Nb(C,N), the $r^*$ of AlN was also calculated by calculating the volume fraction $f$ from the solubility product$^{32}$ and density$^{33}$ of AlN. $r^*(\text{AlN})$ of the Normalized steel was about 12–14 nm, and $r^*(\text{AlN})$ of the Annealed steel was approximately the same, being 10–13 nm. The actually measured particle radius was larger in both the Normalized steel and the Annealed steel. In other words, both the Normalized steel and the Annealed steel satisfied the condition for occurrence of abnormal grain growth. However abnormal grain growth of $\gamma$ occurred in Annealed steel held for 10.8 ks, but was not observed in the Normalized steel in this study as shown in Figs. 5(c) 5(g). Therefore, the effect of spheroidizing annealing before cold forging on abnormal grain growth cannot be explained by the conventional theory based on the pinning effect exerted by nano-precipitate particles.

4.2. Abnormal Grain Growth and Spheroidized Cementite

In the Annealed steel which was immediately quenched from 1203 K, spheroidized cementite with concentrated Cr was observed (Figs. 7(b) and 8). In order to confirm the change of the spheroidized cementite during quasi-carburizing, SEM observation and Cr mapping analysis by EDX were performed. The results are shown in Fig. 11. It became clear that the spheroidized cementite decreases with increasing holding time of quasi-carburizing and disappears after holding for 10.8 ks (Figs. 11(e) 11(j)). Since the occurrence of abnormal grain growth in the Annealed steel was observed after holding for 10.8 ks, the timing of the disappearance of the spheroidized cementite and that of the occurrence of abnormal grain growth are almost the same.

Grain oriented electrical steel sheets$^{34,35}$ are known as a type of steel in which abnormal grain growth is utilized as a microstructure control method. In grain oriented electrical steel sheets, MnS, MnSe, etc. are dispersed as pinning particles, and the particle size of MnS and MnSe$^{36-38}$ is several hundreds nm to several thousands nm, which is the same size as the spheroidized cementite observed in this experiment. Therefore, although the spheroidized cementite is coarse in comparison with the nano-precipitate particles such as Nb(C,N), the dissolution of the spheroidized cementite causes a considerable decrease in pinning force, and the possibility that this promotes abnormal grain growth is suggested.

4.3. Pinning Force Exerted by Spheroidized Cementite

In order to compare the pinning force exerted by the dispersed particles, the pinning energy in materials immediately quenched from the quasi-carburizing temperature was estimated from Eq. (2) by using the modified model of...
Zener and Smith.\textsuperscript{39,40)}

\[ \Delta G_{pin} = \frac{3}{4} \sigma V f^{2/3} \] ........................ (2)

where, \( \Delta G_{pin} \) is the pinning energy, \( \sigma \) is the grain boundary energy, \( V \) is the molar volume, \( f \) is the volume fraction of the particle, and \( r \) is the average particle radius.

The average radius of the spheroidized cementite was measured from SEM images of the immediately quenched Annealed steel (Fig. 11(b)).

The volume fraction of spheroidized cementite in the Annealed steel can be obtained from Eqs. (3) and (4). The ratio of the spheroidized cementite area fraction of the Annealed steel (Fig. 11(a)) and that of the immediately quenched Annealed steel (Fig. 11(b)) was 0.54. The volume fraction of spheroidized cementite in the immediately quenched Annealed steel was estimated by multiplying this ratio (0.54) by the volume fraction of spheroidized cementite in the Annealed steel.

Here, \( C_{total} \) is the C content (0.20\%) of the sample material, \( C' \) is the amount of solid solution of C (0.02\%) in the ferrite, and \( C_{NbC} \) is the amount of C (0.0028\%) as NbC precipitates. \( \rho_{Fe3C} \) and \( \rho_{G} \) are the density of cementite\textsuperscript{39}) and \( \gamma \textsuperscript{31}) \) respectively.

\[
\begin{align*}
    w_{Fe3C} & = \frac{12.01 + 55.85 \times 3}{12.01} (C_{total} - C' - C_{NbC}) \quad \ldots \quad (3) \\
    f_{Fe3C} & = \frac{w_{Fe3C}}{w_{Fe3C} / \rho_{Fe3C} + (100 - w_{Fe3C}) / \rho_{G}} \quad \ldots \quad (4)
\end{align*}
\]

\begin{table}[h]
\begin{tabular}{|c|c|c|c|}
\hline
Nano-precipitates & Spheroidized cementite \\
\hline
\( \rho \) & 2.4 \times 10^{-4} & 5.1 \times 10^{-4} & 1.4 \times 10^{-2} \\
\( r \) & 5.2 \times 10^{-9} m & 4.0 \times 10^{-9} m & 2.5 \times 10^{-7} m \\
\( \sigma \textsuperscript{(4)} \) & 1.0 J/m\textsuperscript{2} & 1.0 J/m\textsuperscript{2} & 1.0 J/m\textsuperscript{2} \\
\( V \) & 7.3 \times 10^{-6} m\textsuperscript{3}/mol & 7.3 \times 10^{-6} m\textsuperscript{3}/mol & 7.3 \times 10^{-6} m\textsuperscript{3}/mol \\
\( \Delta G_{pin} \) & 4.1 J/mol & 0.9 J/mol & 1.3 J/mol \\
\hline
\end{tabular}
\end{table}

Table 2 shows the pinning energies of Nb(C,N), AlN and spheroidized cementite in the immediately quenched Annealed steel. The data used in the calculations are also shown in the table. The pinning energy of spheroidized cementite is 1.3 J/mol and it is larger than the 0.9 J/mol of AlN. The pinning energy of spheroidized cementite is small compared to the 4.1 J/mol of Nb(C,N), but its ratio is about 1/3. In other words, the pinning energy of the spheroidized cementite is not negligible for nano-precipitates such as Nb(C,N) and AlN. As described above, since spheroidized cementite can work effectively as pinning particles, there is a high possibility that it affects abnormal grain growth.

4.4. Dissolution Behavior of Spheroidized Cementite during Quasi-carburizing

Figure 12 shows the phase diagram of the sample steel. This figure was obtained by Thermo-Calc, which is a thermodynamic equilibrium calculation software. Since the quasi-carburizing temperature of 1203 K corresponds to the \( \gamma \) single phase region, it is considered that cementite with concentrated Cr exists in non-equilibrium. In the following, this point is considered from the viewpoint of concentration of Cr in cementite.

Figure 13 shows the relationship between the spheroidized cementite radius and the Cr concentration obtained from the Annealed steel (Figs. 7(b) and 8) immediately quenched after heating in quasi-carburizing (1203 K). Larger spheroidized
cementites had higher Cr content. It is known that Cr concentrates in cementite, and this tendency becomes more pronounced at lower temperatures.\(^{42}\) In addition, since Cr\(_3\)C has a smaller standard free energy of formation than Fe\(_3\)C,\(^{43}\) it is considered that the thermal stability of cementite improves as Cr increases. As a result, spheroidized cementite remained in the Annealed steel even after heating at 1 203 K, and larger spheroidized cementite seems to have higher concentrations of Cr.

In order to investigate the effect of Cr on the dissolution behavior of spheroidized cementite, a dissolution simulation of spheroidized cementite was carried out. For this simulation, DICTRA,\(^{44,45}\) which is a phase transformation analysis software was used. The simulation model is shown in Fig. 14, and the calculation conditions are shown in Tables 3 and 4. The initial Cr content in the spheroidized cementite was set at three levels of 5, 10, and 15% from the content range of the measured values as shown in Fig. 13. The initial radius of the spheroidized cementite was set to 0.27, 0.38, 0.47 \(\mu\)m using the maximum value at each Cr content from Fig. 13. For the Cr content of 15%, in order to compare the effect of the Cr concentration and initial radius, the level of 0.27 \(\mu\)m was added in addition to 0.47 \(\mu\)m. The simulation results are shown in Fig. 15. Cementite having a Cr content of 10% or less and a radius of 0.38 \(\mu\)m or less (Cases 1, 2) disappears after holding for 3.6 ks. On the other hand, cementite having a Cr content of 15% or more and a radius of 0.47 \(\mu\)m or more (Case 3) remains partially even after holding for 3.6 ks and disappears after holding for 10.8 ks. This is approximately in agreement with the observation results shown in Fig. 11. The difference in the dissolution
behaviors in Case 3 and Case 4 with equal Cr contents and different initial radii was more pronounced than that of Case 1 and Case 4 with the same initial radius and different Cr content. From this calculation, it can be said that the effect of the initial radius is dominant over the initial Cr content in the dissolution rate of cementite. From the above results, the concentration of Cr affects the dissolution rate of cementite through the effect on the initial radius of cementite.

Also, since the Cr content in cementite is distributed in a wide range (Fig. 13) of 2 to 18%, the timing of the dissolution and disappearance of the spheroidized cementite also differs greatly, from several minutes to several hours, depending on the spheroidized cementite. As a result, such spheroidized cementite is considered to cause local and non-uniform dissolution behavior. It is considered that such local and non-uniform dissolution behavior of spheroidized cementite promoted the abnormal grain growth of the Annealed steel.

4.5. Mechanism of Effect of Spheroidizing Annealing on Abnormal Grain Growth

Based on the above discussion, the authors summarized the effect of spheroidized cementite in which Cr was concentrated on the abnormal grain growth behavior in the Annealed steel (Fig. 16). Before the occurrence of abnormal grain growth, the driving force of grain growth and the pinning force of the grain boundary are locally balanced at all grain boundaries. The balance relationship between the driving force of grain growth and the pinning force of the grain boundary is influenced by Ostwald ripening of the nano-precipitates or dissolution and disappearance of the spheroidized cementite.

In the Normalized steel, the Ostwald ripening of the nano-precipitates progresses and the pinning force of the grain boundary decreases due to quasi-carburizing up to 1 203 K–21.6 ks. However, since coarsening of precipitates occurs uniformly, there is no local difference in the pinning force of the grain boundary. On the other hand, in the Annealed steel, the pinning force of the nano-precipitates also decreases, in addition, spheroidized cementite in which Cr is concentrated is dissolved during quasi-carburizing. As a result, local and non-uniform decreases occur in the pinning force of the grain boundary, and the balance between the driving force of grain growth and the pinning force of the grain boundary tends to collapse locally. Consequently, some of the crystal grains are coarsened, which causes encroachment of surrounding crystal grains, resulting in abnormal grain growth.

5. Conclusions

As a result of an examination of the effect of spheroidizing annealing before cold forging on abnormal grain growth behavior during carburizing, the following conclusions were obtained.

- In normalized steel without spheroidizing annealing, no abnormal grain growth was observed even after holding at 1 203 K for 21.6 ks. However, abnormal grain growth was observed in the spheroidized annealed steel after holding at 1 203 K for 10.8 ks.
- Spheroidizing annealing does not affect the dispersion state of Nb(C, N) precipitates.
- Spheroidized cementite with concentrated Cr remained in the annealed steel immediately quenched after 1 203 K quasi-carburizing heating. The spheroidized cementite with concentrated Cr dissolved and disappeared with increasing quasi-carburizing holding time.
- Dissolution and disappearance of the Cr concentrated spheroidized cementite occur during quasi-carburizing, so the pinning force of the grain boundary decreases locally and non-uniformly in annealed steel as compared with normalized steel. As a result, abnormal grain growth is likely to occur in the annealed steel.

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Appendix

Effect of Concentration of Mn and Mo on Dissolution Behavior of Spheroidized Cementite

The sample steel of this study contains Mn and Mo as alloying elements other than Cr. Therefore, the effect of Mn and Mo on the dissolution behavior of spheroidized cementite was investigated by DICTRA. The simulation model was equivalent to the model described in the text (Fig. 14), and the calculation was performed under the conditions shown in Tables A1 and A2. Here, the Mn and Mo contents in the cementite were taken as the maximum values obtained by SEM-EDX analysis of 100 spheroidized cementites in the microstructure of the Annealed steel when immediately quenched after quasi-carburizing (1 203 K). Figure A1 shows the simulation results. Even when Mn and Mo are added, the dissolution rate of cementite does not change. As a reason why Mn does not affect the dissolution rate of cementite, it is presumed that the concentration of Cr is up to about 4 times as much as that of Mn, and dissolution of cementite is limited by the Cr. For Mo, the reliability of the simulation result may not be sufficient because there is no reference other than the element in the mobility database (MOB2) used. Since the diffusion coefficient of Mo$^{3+}$ in $\gamma$ is smaller than those of Cr and Mn, the possibility that Mo affects the dissolution behavior of spherical cementite cannot be denied.

REFERENCE


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<th>Table A1. Calculation conditions used with DICTRA.</th>
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<td>Software DICTRA Ver. 26</td>
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<td>Database TCFE7, MOB2</td>
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<td>Temperature 1 203 K</td>
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<th>Table A2. Simulation cases.</th>
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<td>Case No. Chemical compositions</td>
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<td>Spheroidized cementite Cr Mn Mo content</td>
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<tr>
<td>Radius</td>
</tr>
<tr>
<td>--------------------------------------------</td>
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<tr>
<td>Case 3 (Fig.15)</td>
</tr>
<tr>
<td>Cr 15%</td>
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<tr>
<td>5 Fe-0.2%Cr-1.2%Mo</td>
</tr>
<tr>
<td>15 wt% 4 wt%</td>
</tr>
<tr>
<td>0.47 $\mu$m</td>
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<td>Case 5</td>
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<tr>
<td>Cr 15%</td>
</tr>
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<td>6 Fe-0.2%Cr-1.2%Mo</td>
</tr>
<tr>
<td>15 wt% 4 wt%</td>
</tr>
<tr>
<td>0.47 $\mu$m</td>
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Fig. A1. Cementite dissolution behavior obtained by DICTRA.