Structure of the Precipitated Particles at the Third Stage of Tempering of Martensitic Iron-Carbon Steel Studied by High Resolution Electron Microscopy

By Sigemaro Nagakura*, Toshiaki Suzuki*† and Michiko Kusunoki*

Application of the lattice and structure imaging techniques in electron microscopy has shown that $\theta$-$\text{Fe}_3\text{C}$ and $\chi$-$\text{Fe}_5\text{C}_2$ intergrow microsyntactically in the precipitated particles at the early third stage of martensite tempering (520–670 K). Also is found the microsyntactic intergrowth of higher carbides, $\theta_n$-$\text{Fe}_{2n+1}\text{C}_n$, having structures closely related with those of $\theta$-$\text{Fe}_3\text{C}$ and $\chi$-$\text{Fe}_5\text{C}_2$. All the forbidden spots observed in electron diffraction patterns from the precipitates can reasonably be interpreted on the basis of the characteristic growth nature of the carbide phases. At the later stage of tempering (720–870 K), the precipitates are $\theta$-$\text{Fe}_3\text{C}$ containing various kinds of planar defect. A mechanism is presented for the transformation from $\chi$-$\text{Fe}_5\text{C}_2$ to $\theta$-$\text{Fe}_3\text{C}$.

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‡T. Introduction

It is fully established that the final precipitates at the third stage of tempering of martensitic iron-carbon steel is $\chi$-$\text{Fe}_3\text{C}$ (cementite), but there remains a problem whether $\chi$-$\text{Fe}_5\text{C}_2$ (Hågg carbide)$^{(1)-(3)}$ appears or not as the precipitates at the early third stage of tempering (520–720 K). Crangle and Smith$^{(4)}$ suggested the precipitation of $\chi$-$\text{Fe}_5\text{C}_2$ from magnetic study. Ino et al.$^{(5)}$ reported its precipitation from Mössbauer spectroscopy. Application of X-ray diffraction has not been successful to find any clear evidence of the precipitation of $\chi$-$\text{Fe}_5\text{C}_2$.$^{(6)}$ This is because the precipitates are small in size and powder diffraction patterns of $\chi$-$\text{Fe}_5\text{C}_2$ and $\theta$-$\text{Fe}_3\text{C}$ are very similar to each other.

Electron microscopy and selected area diffraction are more advantageous than X-rays for the structural study of fine precipitates. Ohmori and Sugisawa$^{(7)}$, Ohmori$^{(8)}$, and Imai et al.$^{(9)}$ showed single crystalline electron diffraction patterns of the precipitates which could be indexed on the basis of the monoclinic lattice of $\chi$-$\text{Fe}_5\text{C}_2$. However, their diffraction patterns contain many diffraction spots unallowed from the space group of $\chi$-$\text{Fe}_5\text{C}_2$. Kōreda and Shimizu$^{(10)}$, on the other hand, found in their high voltage electron micrographs of the precipitates the images of planar defects parallel to the (001)$_{\theta}$ plane and in the corresponding diffraction patterns streaks running along the [001]$_{\theta}$ direction. They ascribed the planar defects to single $\chi$-$\text{Fe}_5\text{C}_2$ layers formed at random in $\theta$-$\text{Fe}_3\text{C}$ crystals and concluded that the precipitates were not $\chi$-$\text{Fe}_5\text{C}_2$ but faulted cementite. However, a question arises whether their planar defects are really isolated single $\chi$-$\text{Fe}_5\text{C}_2$ layers or not, because the image resolution was not so high.

The lattice and structure imaging techniques in electron microscopy are very useful to study crystal structures and defects. Accordingly, we have applied these methods to investigate the structure of precipitates at the third stage of tempering of martensitic steel. It was found that not only $\theta$-$\text{Fe}_3\text{C}$ and $\chi$-$\text{Fe}_5\text{C}_2$ but also higher carbides having structures closely related with them intergrow microsyntactically$^{(11)}$ in precipitated particles at the early third stage of tempering. This is described in this paper together with other results of observation.

II. Crystal Structures of $\theta$-$\text{Fe}_3\text{C}$, $\chi$-$\text{Fe}_5\text{C}_2$ and Related Higher Carbides

The structure of $\theta$-$\text{Fe}_3\text{C}$ is orthorhombic with lattice parameters $a_{\theta}=0.45248$, $b_{\theta}=...
0.50870 and \( c_\theta = 0.67443 \text{ nm} \) \((12)\), and belongs to the space group \( Pbnm \), while \( \chi\text{-Fe}_3\text{C}_2 \) is monoclinic with lattice parameters \( a_\theta = 1.1562 \), \( b_\theta = 0.45727 \), \( c_\theta = 0.50595 \text{ nm} \) and \( \beta = 97.74^\circ \), and belongs to the space group \( C2/c \) \((13)\). As described by Anderson and Hyde \((14)\), the two structures are closely related with each other. As shown in Fig. 1(a), the coordination polyhedron observed in both the structures is a trigonal prism made of six iron atoms containing one carbon atom at its center, and in the structures such trigonal prisms are linked together to make a prism layer by sharing their corners and edges one another as illustrated in Fig. 1(b).

Figure 2 shows the structure of \( \theta\text{-Fe}_3\text{C} \) projected along the \([100]_\theta \) direction. Two kinds of prism layer, \( A \) and \( B \), which are related by the rotation of \( 180^\circ \) about the normal of prism layer, are stacked in the \([001]_\theta \) direction with a gap of 0.09 nm. The stacking mode can be expressed as \( |A|B|A|B| \cdots \), where the vertical bar indicates the presence of the gap between the prism layers. Since the prism layer has a thickness of 0.25 nm, the stacking period is \( 0.25 + 0.09 = 0.34 \text{ nm} \approx \frac{1}{2} c_\theta \), if we disregard the orientation difference between the \( A \) and \( B \) layers. In the structure of \( \chi\text{-Fe}_5\text{C}_2 \), on the other hand, the two kinds of prism layer are linked together by sharing the prism edges to make a double prism layer, and such double prism layers are stacked with a gap of 0.08 nm as shown in Fig. 3, which is the \([010]_\chi \) projection of the structure. If we denote the double prism layer as \( AB \), the stacking mode can be expressed as \( |AB|AB|AB| \cdots \). Here we disregard the relative displacement among the double prism layers in parallel with the stacking plane. The stacking period is \( 0.25 \times 2 + 0.08 = 0.58 \text{ nm} \approx \frac{1}{4} a_\chi \sin \beta \).

Generalizing the above mode of prism layer stacking, we can make various stacking modes as listed in the fourth column of Table 1. In this table, for example, the stacking mode
Table 1 Stacking modes and periods of a series of carbide phases.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Composition</th>
<th>No. of linked prism layers</th>
<th>Stacking mode</th>
<th>Stacking period (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \theta_1 = \theta )</td>
<td>( \text{Fe}_5\text{C} )</td>
<td>1</td>
<td>( \text{ABA} )</td>
<td>0.34</td>
</tr>
<tr>
<td>( \theta_2 = \chi )</td>
<td>( \text{Fe}_5\text{C}_2 )</td>
<td>2</td>
<td>( \text{ABAB} )</td>
<td>0.58</td>
</tr>
<tr>
<td>( \theta_3 )</td>
<td>( \text{Fe}_4\text{C}_3 )</td>
<td>3</td>
<td>( \text{ABAABAB} )</td>
<td>0.83</td>
</tr>
<tr>
<td>( \theta_4 )</td>
<td>( \text{Fe}_4\text{C}_4 )</td>
<td>4</td>
<td>( \text{ABABABABAB} )</td>
<td>1.08</td>
</tr>
<tr>
<td>( \theta_5 )</td>
<td>( \text{Fe}_{4+1}\text{C}_5 )</td>
<td>5</td>
<td>( \text{ABABABABABAB} )</td>
<td>1.33</td>
</tr>
<tr>
<td>( \theta_n )</td>
<td>( \text{Fe}_{2n+1}\text{C}_n )</td>
<td>( n )</td>
<td>( \text{ABAABABABABA} )</td>
<td>0.25( n )+0.08</td>
</tr>
</tbody>
</table>

* Electron diffraction ** Electron microscopy

\(|\text{ABA}|\text{BAB}|\text{ABA}| \cdots \) made of triple prism layers, ABA and BAB, has the stacking period \( 0.25 \times 3 + 0.08 = 0.83 \text{ nm} \) as shown in the fifth column. The chemical formula of this carbide is \( \text{Fe}_7\text{C}_3 \). The general formula of such higher carbides is \( \text{Fe}_{2n+1}\text{C}_n \) with the stacking period \((0.25n+0.08)\text{ nm}\). In order to save the symbol, we write the higher carbide phase as \( \theta_n \). The \( \theta_1 \) phase corresponds to the cementite phase \( \theta \), and the \( \theta_2 \) phase to the \( \chi \) carbide phase.

All the carbide phases described above are different only in the number of linked prism layers. They make a series of line phases, and therefore, if they appear in the precipitated particles, they may be formed with a common growth axis normal to the stacking plane, in other words, they may intergrow micro-syntactically\(^{11}\).

III. Experimental

Zone refined iron rods (99.99\% pure) and pure iron plates (major impurities: 0.28 wt\%Si and 0.179 wt\%Mn) were cold rolled to a thickness of 0.1 mm, and carburized with methane and hydrogen gas mixture at 1220 K for 0.9–3.6 ks. The carburized plates were austenitized at 1370 K for 0.6–5.4 ks and quenched into iced water followed by immersion in liquid nitrogen. Martensitic iron-carbon steel plates containing 1.0–1.7 wt\%C were obtained. The carbon content was determined from the axial ratio of martensite lattice.

Martensite tempering was done in a vacuum of \( 1 \times 10^{-3} \text{ Pa} \) at 520–870 K for 3.6 ks–7.8 Ms. In order to avoid undesirable diffraction effects from the matrix \( \alpha \)-iron and also as the orientation relationship between the precipitated carbide and the matrix was not the matter of concern, the extraction replica method was applied for specimen preparation. At first, the tempered steel plate was electropolished by the use of a \( \text{H}_3\text{PO}_4-\text{CrO}_3 \) electrolyte kept at 340–350 K until it became thin enough for the electron microscopic observation, and its one side of surfaces was covered by a thin vacuum-evaporated carbon film. Then, the specimen foil thus prepared was immersed in a \( \text{HNO}_3-\text{CH}_3\text{COOH} \) etchant in order to dissolve the matrix \( \alpha \)-iron, and precipitated particles remaining in the carbon film were presented for observation.

The observation was made by the use of JEM-200CX electron microscopes equipped with side and top entry goniometer stages. Photograph 1 reproduces an electron micro-

Photo. 1 Electron micrograph of precipitated particles by tempering at 550 K for 3.6 ks.

\(^{11}\) Crystal structure of orthorhombic carbide \( \text{Fe}_7\text{C}_3 \) found by Eckstrom and Adcock\(^{15}\) and by Kohn and Eckart\(^{16}\) is different from the present structure of \( \theta_2-\text{Fe}_5\text{C}_3 \).
The precipitated particles are observed to line up in parallel with one another. The individual particles are rather plate-like in shape with length of several tens to several hundred nm, width of several tens nm and thickness of 10–20 nm. Diffraction patterns taken from an area of 0.7 µm in diameter and micro-micro diffraction patterns taken from an area as small as 20 nm in diameter in one precipitated particle were almost the same. This shows that the precipitated particles are formed with a definite orientation relationship with the matrix and that the planar defects due to Koreeda and Shimizu are distributed in a region smaller than 20 nm in every particle.

Photograph 2 shows an electron micrograph of a specimen tempered at 870 K for 3.6 ks. The precipitates coalesce to take a spheroidal shape with diameter of several tens to several hundred nm. They are \( \theta \)-Fe\(_3\)C formed with a definite orientation relationship with the matrix. The coalescence proceeds rather rapidly at tempering temperatures above 720 K. It is added that the difference in the purity of source iron, the carbon content of martensite and the tempering period of time did not affect the structure of precipitated particle.

IV. Results

1. Microsyntactic intergrowth of \( \theta \)-Fe\(_3\)C and \( \chi \)-Fe\(_5\)C\(_2\) in the precipitated particles

Photograph 3 reproduces a selected area
electron diffraction pattern of precipitated particles at 670 K, where the incident beam is along the [100]₀ direction. The strong spots can be interpreted as those due to θ-Fe₃C. Besides, streaks running along the [001]₀ direction are observed. Photograph 4 is a one-dimensional lattice image taken with the spots and streaks in the encircled area of Photo. 3. Two kinds of region with different fringe periods are observed. Photograph 5(b) is its enlarged one and is compared with Photo. 5(a), which is the lattice image of θ-Fe₃C giving the fringe period of 0.67 nm corresponding to the lattice spacing of (001)₀. A comparison of these two photographs shows clearly that in some regions of Photo. 5(b) the fringe period is 0.67 nm for the lattice spacing of (001)₀, but in other regions it is 0.57 nm for the stacking period of χ-Fe₅C₂.

The measurement of the fringe periods for θ-Fe₃C and χ-Fe₅C₂ in Photo. 4 showed that they fluctuate in some extent. Figure 4(a) shows the distribution of the fringe periods measured by microdensitometry in the form of histogram. For comparison, the distribution of the fringe period for θ-Fe₃C is given by function (0)l for l=2n+1. Since the standard deviations for the two peaks in Fig. 4(a) are also 0.02 nm, the observed fluctuation of the fringe periods in Photo. 4 are not due to the real fluctuation of stacking periods but due to the granular nature of the recorded images.

Photograph 6 is a structure image of a particle precipitated by tempering at 670 K and taken with the reflections in the encircled area of the inserted diffraction pattern. The incident beam direction is almost parallel to [100]₀ and [010]ₓ. The left- and right-hand side regions are θ-Fe₃C and the central region is χ-Fe₅C₂. The horizontal lines connecting the white dots are kinked at the boundary between θ-Fe₃C and χ-Fe₅C₂ regions, and make an angle of 97° against the [001]₀ direction in accordance with the axial angle β of χ-Fe₅C₂.

The figures shown at the upper part of each region are simulated images calculated by the multi-slice method(18). Parameters used for the image simulations are given in the figure caption†. The white dots correspond to the rows connecting the centers of the trigonal prisms at which carbon atoms exist, and the black regions to the rows of iron atoms, which are unresolved. Agreement between the observed
and simulated images is satisfactory.

The results described above show clearly that $\theta$-Fe$_3$C and $\chi$-Fe$_5$C$_2$ coexist in the precipitated particle in such a way that their prism layers are stacked in parallel with each other, in other words, $\theta$-Fe$_3$C and $\chi$-Fe$_5$C$_2$ intergrow microsyntactically in the precipitated particle at the third stage of martensite tempering. The orientation relationship can be expressed as (100)$_{\chi}$/(001)$_{\theta}$, [001]$_{\chi}$/[010]$_{\theta}$ and [010]$_{\chi}$/[100]$_{\theta}$.

2. Structure of the precipitated particles at the early third stage of martensite tempering

Photograph 7 is a diffraction pattern of precipitated particles formed by tempering at 540 K. Only the reflections from the lattice
planes parallel to the prism layers are excited by inclining the electron beam from the [100]₀ direction towards [010]₀, so that the forbidden spots do not appear. As indicated, the strong spots are indexed as the 00l reflections of $\theta$-Fe₃C and the medium strong spots as the h00 reflections of $\chi$-Fe₅C₂. Their intensities coincide with the calculated ones for the respective carbides. Besides, very weak spots are observed with distances corresponding to the lattice spacings 0.159 and 0.146 nm. As shown in Table 1, the sixth column, 0.159 × 7 = 1.12 nm is almost equal to the stacking period of the higher carbide $\theta_2$-Fe₉C₄, 1.08 nm, and 0.146 × 9 = 1.32 nm is almost equal to the stacking period of $\theta_5$-Fe₁₁C₅.

Photograph 8 reproduces a lattice image of a particle precipitated by tempering at 540 K. $\theta$-Fe₃C and $\chi$-Fe₅C₂ are observed to intergrow microsyntactically in the precipitated particle with thickness of 10 nm at most. Beside these, we can observe thin layers with long fringe periods, which are 0.8 and 1.1 nm. They correspond respectively to the stacking period of $\theta_3$-Fe₇C₃, 0.833 nm, and that of $\theta_4$-Fe₉C₄, 1.08 nm, as shown in the seventh column of Table 1.

From the results described above, we can say that the carbides $\theta_\text{n}$-Fe₂ₙ₊₁Cₙ are formed microsyntactically in the precipitated particles at the early third stage of martensite tempering. The higher carbides with $n$ larger than 3 are thin with thickness 5 nm at most, and disappear gradually with increasing tempering temperature. Since the most stable carbide is $\theta$-Fe₃C and the next is $\chi$-Fe₅C₂, it is supposed that the stability of carbide decreases with increasing $n$. 
3. Structure of the precipitated particles at the later third stage of martensite tempering

Above 720 K, the coalescence of precipitates takes place and $\theta$-Fe$_3$C particles are formed. They contain various kinds of defect in the stacking of prism layers in the structure. Some examples are shown in the following.

Photograph 9 is a lattice image of a precipitated particle formed by tempering at 870 K. The number of fringes is less by one in the inside region than in the outside region, and the image contrast due to the mismatch in the stacking of prism layers is observed. Figure 5 illustrates a possible structure.

Photograph 10 reproduces a lattice image showing thin layers of $\chi$-Fe$_5$C$_2$ composed of two double prism layers, which terminate in the structure of $\theta$-Fe$_3$C. A slight increase in the image contrast is observed at the ends of the $\chi$-Fe$_5$C$_2$ layers. This indicates that the lattice is strained there.

Photograph 11 is an image of a defect probably formed at the time of coalescence of precipitated particles. A structural model is illustrated in Fig. 6, where the stacking of triple prism layers as $|B|ABB|A|\cdots$ is assumed by considering the fringe spacings and positions in Photo. 11. In the stacking mode of prism layers, the stacking mode made of the same kind of prism layers such as $|A|A|\cdots$, $|AA|AA|\cdots$ etc. is possible. For example, the stacking mode $|AA|AA|\cdots$ produces a monoclinic structure belonging to the space group $Cc$, which has no center of symmetry.
V. Discussion

In the present study, it was shown by the high resolution electron microscopic observations that not only $\theta$-Fe$_3$C and $\chi$-Fe$_5$C$_2$ but also the higher carbides $\theta_n$-Fe$_{2n+1}$C$_n$($n \geq 3$) intergrow microsyntactically in the precipitated particles at the early third stage of tempering of martensitic iron-carbon steel and that they transform gradually to $\theta$-Fe$_3$C at the later stage of tempering above 720 K. The structure of the precipitated particles at the early third stage somewhat resembles that of a faulted cementite found by Koreeda and Shimizu(10), but the amount of $\chi$-Fe$_5$C$_2$ is not always less than that of $\theta$-Fe$_3$C as was seen in Photo. 8. Therefore, the name “faulted cementite” is not considered to be appropriate to represent the structure of precipitates.

The existence of the higher carbides $\theta_n$-Fe$_{2n+1}$C$_n$ was proved by the present study. Their crystal structures, however, have not been fully established. In order to analyse the structures, application of the structure imaging technique is considered to be most appropriate. Along this line, a study is now in progress.

Photograph 12 is an electron diffraction pattern taken under the same condition as Ohmori(8). He interpreted this pattern as that
of $\chi$-Fe$_3$C$_2$ taken with the beam incident along [111]$_\theta$ and considered it as one of the evidences of the precipitation of $\chi$-Fe$_5$C$_2$ at the early third stage. However, this pattern contains many forbidden spots $hkl(h+k=2n+1)$ and $h0l(h=2n+1)$ as indicated by crosses in Fig. 7, and they cannot be interpreted by double diffraction of the allowed reflections for $\chi$-Fe$_5$C$_2$ shown by solid circles. The carbides $\chi$-Fe$_5$C$_2$ and $\theta$-Fe$_3$C are grown microsyntactically in the precipitated particle and the [111]$_\chi$ direction is almost parallel to [112]$_\theta$.

The diffraction spots due to $\theta$-Fe$_3$C under the [112]$_\theta$ beam incidence appear at the positions as indicated by open circles in Fig. 7 and some of them overlap with the spots due to $\chi$-Fe$_5$C$_2$. As schematically illustrated in Fig. 8, the incident beam passes through both the $\theta$-Fe$_3$C and $\chi$-Fe$_5$C$_2$ layers in the case of Photo. 12 because the prism layers incline to the electron beam. Therefore, double diffraction takes place from the two kinds of carbide layer. This interprets the appearance of all the diffraction spots in Photo. 12. Photograph 13 is a dark field electron micrograph taken with the 101$_\theta$ and 101$_\chi$ spots overlapped in Photo. 12 (encircled). Since the spacings and orientations of their reflecting planes are slightly different from each other, Moiré fringes are produced by double diffraction from them. All the anomalous spots in diffraction patterns taken with various incident beam directions can reasonably be interpreted by considering the microsyntactic intergrowth of $\theta$-Fe$_3$C, $\chi$-Fe$_5$C$_2$ and the higher carbides $\theta_n$-Fe$_{2n+1}$C$_n$.

![Fig. 8 Geometrical relationship between the incident electron beam and the $\theta$-Fe$_3$C and $\chi$-Fe$_5$C$_2$ layers.](image)

![Photo. 13 Dark field electron micrograph taken with the encircled spot 201$_\theta$-202$_\chi$ in Photo. 12.](image)

![Fig. 9 Transformation mechanism of $\chi$-Fe$_5$C$_2$ to $\theta$-Fe$_3$C. (a) [001]$_\chi$ projection of the structure of $\chi$-Fe$_5$C$_2$. Solid circles represent carbon atoms. (b) Same as (a), but the carbon atoms are moved to the positions represented by open circles and isolated prism layers are newly formed. (c) [010]$_\theta$ projection of the structure of $\theta$-Fe$_3$C.](image)
The carbides $\chi$-Fe$_5$C$_2$ and $\theta_n$-Fe$_{2n+1}$C$_n$ transform gradually to $\theta$-Fe$_3$C with the progress of tempering. The transformation mechanism is considered as follows. For simplicity, we consider the case of the transformation from $\chi$-Fe$_5$C$_2$ to $\theta$-Fe$_3$C. Figure 9(a) is the structure of $\chi$-Fe$_5$C$_2$ projected along the [001]$_\chi$ direction, where the solid circles represent carbon atoms. As shown in (b), if the carbon atoms move to the positions represented by the open circles, new trigonal prisms represented by the broken lines are formed, and the structure made of double prism layers changes to a structure made of single prism layers. The structure of $\theta$-Fe$_3$C shown in (c) is completed by the displacement of iron atoms in the [001]$_\theta$ direction together with slight displacements in the [100]$_\theta$ and [010]$_\theta$ directions. Excess carbon atoms in $\chi$-Fe$_5$C$_2$ for this transformation may diffuse away towards the surface of the precipitated particle and contribute to the growth of $\theta$-Fe$_3$C particle. Since this structural change does not require a long distance diffusion of iron atoms, the transformation is of in-situ type and not accompanied by an appreciable change in the external shape and the volume. The heat evolution observed in a specific heat vs temperature curve in a temperature range from 520 to 770 K$^{(20)}$ can partly be ascribed to such a transformation.

As reported previously$^{(21)-(23)}$, the carbide precipitated at the first stage of martensite tempering is $\eta$-Fe$_3$C. A study to find the relation between the precipitates at the first stage and the third stage is important. The result of study will be reported in a near future.

Acknowledgments

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