Microstructural Evolution and Carbides in Quenched Ultra-low Carbon (Fe–C) Alloys

Dehai PING,1)* Tianwei LIU,1) Masato OHNUMA,2) Takahito OHMURA,1) Taichi ABE1) and Hidehiro ONODERA1)

1) National Institute for Materials Science, Sengen 1-2-1, Tsukuba, Ibaraki, 305-0047 Japan.
2) Faculty of Engineering, Hokkaido University, Kita 13 Nishi 8, Kita-ku, Sapporo, Hokkaido, 060-8628 Japan.

(Received on October 26, 2016; accepted on March 13, 2017; J-STAGE Advance published date: May 19, 2017)

Binary Fe–C alloys are basic for various carbon steels in view of chemical compositions, thus, understanding the microstructural evolution in Fe–C alloys is fundamentally necessary. Three Fe-xC (x = 0.02, 0.05 and 0.1 wt.%) alloys were selected and the microstructure changes during water-quenching process has been studied using transmission electron microscopy (TEM).

Fine carbides with a size of tens of nanometer, mainly Fe3C cementite, are observed in quenched Fe-0.02C and Fe-0.05C samples. Lath martensite has been commonly observed in all the quenched alloys. Body-centered cubic (bcc) (112) < 111 >-type twinning structure with fine particles on the twinning boundaries has been frequently observed in the quenched Fe-0.1 wt.%C samples; while the fine cementite are absent in the twinned region.

A novel formation mechanism for the quenched microstructure has been proposed as follows: 
Austenite → twinned martensite (bcc + α on twinning boundaries) → lath martensite + carbides on lath boundaries → carbides + ferrite (α-Fe). The first transition corresponds to the martensitic transformation; while the second and third transitions are the auto-tempering results of the first one. In the ultra-low carbon sample (Fe-0.02C), the third transition will be the observed microstructure; Slight high carbon (Fe-0.05C) will result in the second transition, not to the third one. The product of the first transition will be the twinned martensite (Fe-0.1C), and the final microstructure will not experience the second and third transitions. Of course, the quenching condition can also affect the final microstructure.

KEY WORDS: steel; lath martensite; carbides; twinning; TEM.

1. Introduction

In dilute Fe-C alloys, carbon atoms have been traditionally postulated to partition into the octahedral interstitial sites of α-Fe, which has a body-centered cubic (bcc) crystal structure, during quenching from high austenitization temperatures.1–11) Upon quenching, both Ms (martensite start temperature) and Mf (martensite finish temperature) decrease with the increasing of carbon content, and also the Ms decreasing rate is faster than that of Mf.7,12,13)

The interstices in iron are of two types, surrounded respectively by a tetrahedron of 4 atoms and by an octahedron of 6 atoms.14) Atomic radius of carbon is commonly recognized as ~0.67Å (there is no method to measure the radius of a single atom accurately). The largest radius of the interstitial sites in α-Fe is the octahedral site and it is about 0.36Å; while the largest one in γ-Fe is about 0.52Å. Thus, considering the space diameter of the interstitial sites, it is difficult for carbon atoms to stay in the interstitial sites of α-Fe. Nevertheless, carbon atoms have been suggested to occupy the octahedral interstitial sites in α-Fe and assumed that the carbon atoms into the octahedral sites will produce a large anisotropic strain in the surrounding matrix since the octahedron in α-Fe is distorted compared with that in γ-Fe.5–10) Hence the solubility of interstitial atoms in α-Fe is very small.

Such geometrical consideration suggests that it is difficult to incorporate carbon atoms into the interstices in an ideal α-Fe lattice. In general, ferrite is the α-Fe grain having a carbon content less than 0.02 wt.%. The very small carbon solubility in α-Fe measured by experimental methods could be due to some undetected ultra-fine carbides or carbon atoms trapped at grain boundaries and/or dislocation defects or experimental errors. Experimental measurements have revealed that the maximum carbon in α-Fe is about 0.02 wt.%.20,21) This corresponds to one carbon atom per ~500 unit cells of α-Fe, or one carbon atom in a 2.21 nm3 cubic volume.

If the carbon atoms can solid solution into α-Fe and makes α-Fe lattice distorted, then, no any carbides should be observed in quenched Fe–C alloys with a low carbon content (0.02–0.1 wt.%). A traditional explanation about the carbide formation in ultra-low carbon quenched Fe–C alloys is attributed to the auto-tempering process. However, no explanation about the dependence of the carbide formation on the carbon content.
formation on the carbon content in Fe–C alloys, or below which carbon content, there is carbide formation due to auto-tempering; above which carbon content, the auto-tempering will have no effect on the carbide formation. For this purpose, the quenched microstructure in the Fe–C alloys with the carbon content from 0.02 to 0.1 (wt.%) will be investigated using transmission electron microscopy (TEM) in the present investigation. The second purpose of this investigation is aimed at exploring the dependence of the bcc $\{112\} <111>$-twinning formation on the carbon content in the Fe–C binary alloy system upon quenching. In general, dislocations are recognized as a main substructure in martensite in quenched low carbon steels; while the $\{112\} <111>$ twinning structure is in quenched high carbon steels.22)

2. Experimental Procedure

Three 10 kg Fe-0.02C, Fe-0.05C and Fe-0.1C (wt.%) ingots were prepared in a high vacuum induction furnace under Ar atmosphere. The ingot was solution treated at about 1 200°C for 2 h and then hot forged into a thick plate with a thickness of about 20 mm. Inductively coupled plasma-optical emission spectrometry (ICP-OES) (Shimadzu ICPS-720) was used for chemical analysis and the results are shown in Table 1. A small plate with the size of about 10 mm × 10 mm × 1.5 mm was then mechanically cut from the 20 mm thick plate, such small plate was directly put into a furnace at various austenitized temperatures, and then oil-quenched or water-quenched. The quenching condition is listed in Table 2.

The specimen for TEM observation was prepared from the water-quenched thin plates (~10 mm × 10 mm × 1.5 mm) by mechanical grinding and polishing, and finally ion-milled at room temperature. The microstructural observation was carried out with a JEM 2000FX TEM operated at 200 kV and a JEM 2100F TEM operated at 200 kV.

### Results

3.1. Fe-0.02wt.%C

Figure 1 shows typical TEM bright field image obtained from the oil-quenched Fe-0.02C sample. A typical lath-like martensite structure, which is normally called as lath martensite, is commonly observed. All the grains are α-Fe ferrite with a high density of dislocation-like contrast within the grains. The lath width is at several hundreds of nanometer scale or one micron.

Figure 2 shows the TEM bright field images obtained from the oil-quenched Fe-0.02wt.%C sample. Fine particles with tens of nanometer size can be clearly seen in the martensite. The ion-milled TEM specimen has been cleaned using ion-milling cleaner to confirm that those fine particles are not due to artifact produced during the specimen preparation. Such fine particles seem to be randomly distributed and the size is about 20 nm or less, which can be clearly seen in the enlarged image shown in Fig. 2(b).

3.2. Fe-0.05wt.%C

Figure 3 shows general TEM bright field image obtained from the water-quenched Fe-0.05wt.%C sample after austenitized at 950°C for 30 min. Fine particles with its average size of 50 nm can be clearly seen. Increasing the austenitizing temperature up to 1 100°C, no much difference can be observed, and a possible particle size reduction may happen if the austenitizing temperature increases.

<table>
<thead>
<tr>
<th>Sample (wt.%)</th>
<th>Quenching condition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-0.02C</td>
<td>1 200°C/1 h, oil-quenching</td>
</tr>
<tr>
<td>Fe-0.05C</td>
<td>950°C/30 min, water-quenching</td>
</tr>
<tr>
<td>Fe-0.05C</td>
<td>950°C/2 h, water-quenching</td>
</tr>
<tr>
<td>Fe-0.1C</td>
<td>1 100°C/1 h, water-quenching</td>
</tr>
<tr>
<td>Fe-0.1C</td>
<td>950°C/30 min, water-quenching</td>
</tr>
<tr>
<td>Fe-0.1C</td>
<td>950°C/2 h, water-quenching</td>
</tr>
<tr>
<td>Fe-0.1C</td>
<td>1 100°C/1 h, water-quenching</td>
</tr>
</tbody>
</table>

Table 1. Chemical analysis results (wt.%).

<table>
<thead>
<tr>
<th>Sample</th>
<th>C</th>
<th>N</th>
<th>Si</th>
<th>P</th>
<th>S</th>
<th>Mn</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-0.02wt.%C</td>
<td>0.018</td>
<td>0.002</td>
<td>0.007</td>
<td>&lt;0.005</td>
<td>&lt;0.002</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>Fe-0.05wt.%C</td>
<td>0.047</td>
<td>0.001</td>
<td>0.003</td>
<td>&lt;0.005</td>
<td>&lt;0.002</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>Fe-0.1wt.%C</td>
<td>0.088</td>
<td>0.003</td>
<td>0.005</td>
<td>&lt;0.005</td>
<td>&lt;0.002</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
</tr>
</tbody>
</table>

Fig. 1. A typical TEM bright field micrograph showing the martensitic lath structure in the oil-quenched Fe-0.02wt.%C sample after austenitized at 1200°C for 1 h.

Fig. 2. Microstructure in the oil-quenched Fe-0.02wt.%C sample. (a) TEM bright field micrograph revealing fine particles in martensitic laths. (b) An enlarged image of the region outlined by dashed square lines in (a).
By prolonging the austenitizing time to 2 hours, the carbide size seems to be larger than that in the sample treated for 30 min. The selected area electron diffraction (SAED) patterns analysis from those carbide particles have been carried out on the water-quenched Fe-0.05C sample after austenitized at 950°C for 2 h. One of the carbide particles ((a)) and its corresponding SAED pattern ((b)) are shown in Fig. 4. Since the fine particle size is much smaller than that of the selective aperture diameter (~450 nm), the diffraction spots shown in Fig. 4(b) from the matrix are inevitably included in the SAED pattern. Except for the fundamental diffraction spots from α-Fe, the extra diffraction spots can be indexed as θ-type Fe₃C cementite (orthorhombic; \(a = 4.518 \text{ Å}, b = 5.069 \text{ Å}, c = 6.736 \text{ Å}\)). These cementite particles are normally having the following crystallographic orientation relationship with α-Fe: \([011]_\text{α} \parallel [101]_\theta\) and \([111]_\text{α} \parallel (010)_\theta\). The present observed orientation relationships match well with the previous reported one.23)

In the quenched Fe-0.05wt.%C samples, the lath martensite structure has been commonly observed as shown in Fig. 5(a). The lath width is at several hundreds of nanometer scale or one micron size. It is difficult to see the detail structure at the lath boundaries as shown in Fig. 5(a); however, when the TEM specimen was tilted, the carbides contrast can be clearly seen at the lath boundaries as shown in Figs. 5(b) and 5(c). Those carbides, looks like inside the grains, are actually located at sub-grain boundaries or lath boundaries, which can be confirmed by the tilting experiment observations. The present tilting experiment (tilting the TEM specimen during TEM observations) suggests that all carbides are located at boundaries (lath boundaries or sub-grain boundaries). It is difficult to say that some carbide particles are inside a single α-Fe crystal since there is a high density of dislocation-like boundaries. An isolated particle in the observation direction may actually connect to some boundaries after the TEM specimen was tilted.

### 3.3. Fe-0.1wt.%C

Figure 6 shows a typical TEM bright field micrograph obtained from the oil-quenched Fe-0.1wt.%C samples. The lath-type martensitic structure is the main microstructure feature, and most of the martensite shows twinning contrast in the observation direction. The twinning contrast (the straight line contrast in the picture) can also be seen in some martensitic laths after the TEM specimen was tilted. Thus, the twinning contrast can be seen in almost all martensitic laths. However, no twin can be observed in other heat-treated and water-quenched Fe-0.1C samples.

Figure 7(a) is a TEM bright field image revealing a twinning contrast in one martensitic lath. The corresponding SAED pattern is shown in Fig. 7(b). The diffraction pattern was observed with the electron beam parallel to the \([011]_\text{α} \parallel \text{Fe zone axis}\). The detail diffraction spots analysis can be seen from Figs. 7(g)–7(i). The α-Fe fundamental diffraction spots are outlined with the dashed lines. Figures 7(g) and 7(h)
have a \{112\} <111> -type twinning relationship. In Fig. 7(b), there are some extra diffraction spots in addition to the diffraction spots from the twinning structure. These extra diffraction spots can be explained by a metastable \(\alpha\)-Fe phase as shown in Fig. 7(i).\(^{24-26}\) The corresponding dark field images (Figs. 7(c) and 7(d)) obtained using the \(\alpha\)-Fe diffraction spots clearly show that the fine \(\alpha\)-Fe particles are at the twinning boundaries.

**Figure 8** is a high resolution TEM image taken from the above twinned martensite region. Figures 8(b)–8(d) are the Fast Fourier Transformed (FFT) images obtained from the corresponding b, c and d regions, respectively. In Fig. 8(d), the FFT diffraction spots correspond only to the [011] zone axis diffraction spots of \(\alpha\)-Fe phase; while the images from b and c regions show the \(\alpha\)-Fe diffraction spots and \(\alpha\)-Fe spots. Those \(\alpha\)-Fe diffraction spots are from the three regions with a stacking fault-like contrast in the whole image (Fig. 8(a)). By looking at the left down corner carefully, one can find a tiny twin crystal inside the \(\alpha\)-Fe phase. This thin plate of twin crystal is shown in **Fig. 9**.

The TEM observation results have confirmed that the \{112\} <111>-type twinning structure is definitely observed in the martensite of the quenched Fe-0.1wt.%C samples, and the twinning structure is clearly a substructure in the martensite instead of dislocations as a main substructure in the low-carbon martensitic laths.

Various quenching conditions have been carried out on the Fe-0.1wt.%C alloy, and the substructure in the martensitic lath is more or less similar with that shown in Figs. 6 and 7. One more important point is that the fine \(\theta\)-type Fe\(_3\)C cementite particles are less commonly observed. It turns out that once twinned martensite forms; the Fe\(_3\)C cementite or carbide particles will be absent.

![Fig. 6. TEM bright field micrograph revealing high density of twinning structure in the oil-quenched Fe-0.1wt.%C sample after austenitized at 1 200°C for 1 h. No carbides can be observed in twinned region.](image)

![Fig. 7. TEM results revealing that a \{112\} <111>-bcc twinning structure commonly appears in the martensite of the oil-quenched Fe-0.1wt.%C sample after austenitized at 1 200°C for 1 h. All dark field images have the same scale bar as shown in (a). (Online version in color.)](image)
4. Discussion

4.1. Auto-tempering

The experimental measurement of elastic relaxation suggested that the solubility of carbon in \( \alpha \)-Fe can be 0.0197 wt.% at 713°C down to 0.0022 wt.% at 444°C by quenching the samples at various temperatures, at which gas carburization process was carried out.\(^{27}\) In a recent electrical resistivity measurement at 4.2 K, the results have also suggested that the carbon solubility in high purity of \( \alpha \)-Fe is low, at about one tenth of a mass ppm. It is about 0.005 wt.% at 600°C and much less at low temperatures.\(^{28}\)

From the Fe–C phase diagram, the carbon solubility can reach up to 2.17 wt.% in \( \gamma \)-Fe at austenite temperature region.\(^{29}\) Thus, the amount of carbon atoms in the present studied alloys can be fully dissolved into \( \gamma \)-Fe. After quenching, except for the amount of solubility of carbon atoms if there was in \( \alpha \)-Fe, the extra carbon atoms have to stay outside of \( \alpha \)-Fe. The question comes out about where should the carbon atoms go? A newly found metastable \( \chi \)-Fe phase may answer this question.\(^{24–26}\) At the Ms — Mf temperature interval, the carbon atoms can incorporate into the \( \chi \)-Fe phase, which has a primitive hexagonal structure and special orientation relationships with \( \alpha \)-Fe.

Based on the lattice parameter relationship of \( a_{\chi} = \sqrt{2} \times a_{\text{bcc}} \) and \( c_{\chi} = \sqrt{3}/2 \times a_{\text{bcc}} \), the smallest radius of the octahedral interstitial site in \( \chi \)-Fe structure can be 0.187 \( a_{\text{bcc}} \).\(^{24,30}\) Then, it is about 0.53 Å for \( a_{\text{bcc}} = 2.85 \) Å. The smallest radius of the octahedral interstitial site in \( \omega \)-Fe structure is almost equal to that in \( \gamma \)-Fe, much larger than that in \( \alpha \)-Fe. Thus, carbon atoms can stay in the \( \omega \)-Fe instead of \( \alpha \)-Fe when \( \gamma \)-Fe disappears. The theoretical calculation results have suggested that the \( \omega \)-Fe occurs as the lowest energy barrier in the \( \gamma \)-Fe \( \rightarrow \) \( \alpha \)-Fe pathway, however, the \( \omega \)-Fe is

![Fig. 8. High resolution TEM results revealing a relationship of \( \omega \)-Fe structure and \( \alpha \)-Fe in the above twinning region shown in Fig. 7. (Online version in color.)](image)

![Fig. 9. High resolution TEM image enlarged from the left down corner in Fig. 8(a). A thin twin crystal of \( \alpha \)-Fe structure can be seen clearly. The twin is surrounded by \( \omega \)-Fe phase contrast. (Online version in color.)](image)
dynamically unstable.\(^24,31–35\) When carbon atoms join in the \(\alpha\)-Fe structure, the \(\omega\)-Fe(C) particles can be stabilized at the twinning boundaries and observed at room temperature after quenching.

We can try to understand the auto-tempering process in the following way. Once the temperature reaches down to \(M_s\), which means the transformation from \(\gamma\)-Fe to \(\alpha\)-Fe, \(\omega\)-Fe and \(\alpha\)-Fe will form simultaneously, and the carbon atom incorporates into the \(\omega\)-Fe.\(^33\) In ultra-low carbon Fe–C alloys, the \(M_s\) and \(M_f\) are normally at high temperature around 500°C. The metastable \(\omega\)-Fe(C) formed at such high temperature will immediately transform into FeC cementite or any other carbides,\(^36,37\) which means auto-tempering behavior happens. Attention should be paid to the carbon concentration in \(\omega\)-Fe. One \(\omega\)-Fe unit cell has three iron atoms, once one carbon atom comes into the \(\omega\)-Fe unit cell; then, the carbon concentration in the \(\omega\)-Fe(C) immediately becomes 25 at.% which is the exact carbon concentration in FeC. We cannot assume any carbon concentration less than 25 at.% in the \(\omega\)-Fe(C) phase theoretically, which means that we cannot assume half a carbon atom stays in one \(\omega\)-Fe(C) unit cell or one carbon atom stays in two \(\omega\)-Fe(C) unit cells when theoretical calculation is considered.

Compared with the \(M_s\) in Fe-0.02C (wt.%) alloys, the \(M_s\) in Fe-0.1C (wt.%) alloys is lower, thus, the \(\omega\)-Fe(C) formed at the low temperature will be difficult to transform into FeC cementite. The \(\omega\)-Fe(C) will remain as it is at the \{112\} <111> twinning boundaries. In the Fe-0.02C (wt.%) alloys, the absent of the twinning structure could be another reason for inducing the \(\omega\)-Fe(C) → carbide or cementite transform since that the twinning boundary structure and the \(\omega\)-Fe(C) seems to stabilize each other. In bcc metals and alloys, the \{112\} <111> twinning has been considered as a \(\omega\) → bcc phase transition product and the \(\omega\) structure or phase remains at the \{112\} <111> twinning boundary region.\(^25,38\) Although the \(\omega\) phase formed from bcc metals and alloys is having the same crystalline structure with the present discussed \(\omega\)-Fe, which is formed from fcc-Fe, the bcc \{112\} <111> twinning mechanism in quenched carbon martensite is different from that in bcc metals and alloys.\(^33,38,8\)

Recent research results published by Yonemura et al. have revealed that the \(\gamma\)-Fe → \(\alpha\)-Fe solid-solid transformation can happen at around 600°C for Fe-0.02C (wt.%).\(^39\) Such temperature was measured using an \textit{in situ} two-dimensional time-resolved X-ray diffraction on the directional solidification process during fusion welding, in which the cooling rate can be controlled. The welding process is a classic example where high cooling rates take place. While in the measured Fe-0.88C (wt.%), the \(\gamma\)-Fe → \(\alpha\)-Fe solid-solid transformation temperature was as high as 700°C, which is much higher than that of the low-carbon alloy. It is difficult to understand that the \(\gamma\)-Fe → \(\alpha\)-Fe transformation temperature in Fe-0.02C (wt.%) is lower than that in Fe-0.88C (wt.%) in the literature.\(^39\) One of the reasons could be the measurement temperature point. At around 700°C, the authors probably did not measure the diffraction of the Fe-0.02C (wt.%) alloy. By the way, no body-centered tetragonal (BCT) martensitic structure was detected at 700°C in the quenched Fe-0.88C (wt.%); sample; and the 200\(\alpha\)-Fe and 211\(\alpha\)-Fe don’t show any peak splitting even at low temperature. Many weak diffraction rings, which have been ascribed to the FeC cementite by the authors, can be seen around the 211 peak. Anyway, the results presented in the literature experimentally suggested that the \(\gamma\)-Fe → \(\alpha\)-Fe solid-solid transformation can happen at high temperature even in the high carbon Fe-0.88C (wt.%) alloys, which is significantly different with the value of commonly accepted \(M_s\).\(^7\)

Auto-tempering has been traditionally applied for explaining the carbide formation in the quenched low carbon Fe–C alloys. The carbon atoms incorporate into the \(\alpha\)-Fe during the phase transformation, and then carbides precipitate out from the \(\alpha\)-Fe matrix during further cooling. For the secondary phase precipitated out from the matrix, the secondary particles normally have the same crystallographic orientation relationship with the same matrix. However, as can be seen in the TEM micrographs (Fig. 2), the carbides seem to be randomly orientated each other even for the nearby particles.

The direct reason for the carbides precipitated out from the matrix during auto-tempering could be the size of the interstitial space, which shrinks at low temperature. We can assume the precipitation starting temperature as \(T_p\), which can be any temperature below \(M_s\). This \(T_p\) means that the carbon atoms will be difficult to incorporate into the interstitial sites of \(\alpha\)-Fe. At least, below \(T_p\), the amount of carbon atoms coming out from the matrix is larger than that going into the matrix. As well-known that the \(M_s\) decreases when the carbon content increases in the Fe–C alloys during quenching. Thus, we can compare the two Fe–C alloys with different carbon content as explained in Fig. 10. The two alloys can be quenched together in order to keep the exact same cooling rate, thus, the red line, which corresponds to the cooling curve in both figures, can be exactly the same. The \(T_s\) can be any temperature between \(M_s\) and room temperature (RT). As carbon content increase, the \(M_s\) is also gradually decreasing. Anyway, we can find that the \(M_s\) of one Fe–C alloy is lower than the \(T_p\) in the low carbon Fe–C alloy. In such a case, when we quench that Fe–C alloy with low \(M_s\), we should only have \(\alpha\)-Fe instead of carbon-enriched martensite. However, such an assumption is opposite to all experimental results, which means auto-tempering explanation is not true for the carbide formation in the quenched low-carbon containing Fe–C alloys. If \(T_p\) is between \(M_s\) and \(M_f\), carbides can also form during the auto-tempering while the sample is cooling down.

\(M_s\) temperature can be estimated based on the following

![Fig. 10. Comparison between the two Fe–C alloys with different carbon content during quenching at the same cooling rate. (Online version in color.)](image)
4.2. A Novel Formation Mechanism of Lath Martensite

The lath martensite can be observed in all the investigated Fe–C alloys with the carbon content as low as 0.02 wt.%. Such kind of result is not exciting since the lath martensite has been reported to form even in a pure iron after quenching. The lath martensitic microstructure formation depends on the cooling rate and/or heat treatment condition (temperature and time) at the austenitization temperature. Higher cooling rate can easily result in the lath martensitic formation regardless of the carbon content.

As revealed in Figs. 6 & 7, the \{112\}<111>-type twinning structure is the common substructure of martensite in the quenched Fe-0.1C alloy. Be aware of that the twinning plane is \{112\} planes, which mean that all the interfaces between a twin crystal and the surrounding matrix are \{112\} planes. As discussed in the previous publication, once the martensitic transformation starts, the \{112\}<111>-type twinning structure will automatically form. Actually, the martensitic transformation can be ascribed to the \{112\}<111>-type twinning formation. Our previous experimental observations also confirmed that the metastable \(\alpha\)-Fe phase formed at the twinning boundaries, and theoretical calculation results suggested that the carbon atoms can stabilize the \(\alpha\)-Fe phase, thus, the metastable \(\alpha\)-Fe phase can be written as the \(\alpha\)-Fe(C) phase in carbon steels.

A complete \(\gamma\rightarrow\alpha\) solid-solid transformation pathway in iron has been explained in detail in a previous publication. As revealed in Figs. 6 & 7, the \{112\}<111>-type twinning plane is \{112\} planes, which mean that all the interfaces between a twin crystal and the surrounding matrix are \{112\} planes. As discussed in the previous publication, once the martensitic transformation starts, the \{112\}<111>-type twinning structure will automatically form. Actually, the martensitic transformation can be ascribed to the \{112\}<111>-type twinning formation. Our previous experimental observations also confirmed that the metastable \(\alpha\)-Fe phase formed at the twinning boundaries, and theoretical calculation results suggested that the carbon atoms can stabilize the \(\alpha\)-Fe phase, thus, the metastable \(\alpha\)-Fe phase can be written as the \(\alpha\)-Fe(C) phase in carbon steels.

![Fig. 11.](image)

![Fig. 12.](image)
The twin crystals will be dissolved into the matrix and/or Fe₃C carbides during the auto-tempering process. Once the transformation finished, the martensitic lath structure can be formed with the carbides at the lath boundaries as revealed in Fig. 12(c). When the auto-tempering temperature is high enough (for example, in the Fe-0.02C alloy), then the carbides can become much larger and well-separated as shown in Fig. 12(d). The twinned crystals are fully disappeared, the total matrix becomes one ferrite grain with the contrast of dislocation-like misfit boundaries (or sub-grain boundaries) in it.

In the 1960s, M. G. H. Wells observed that the cementite particles prefer to form on the {112} fine twinning planes instead of grain boundaries in a tempered Fe–Ni–C alloy, and also the cementite particles are composed of fine rods or needles parallel with the [010]Fe₃C and <111>α-Fe direction. Such experimental results match well with the above discussion.

In Fig. 12(d), three regions marked by A, B and C reveal that the crystal lattice in A, B and C cannot perfectly match together at the boundary region. Thus, the A/B and B/C lattice misfit boundaries will appear as shown by the curved lines, which terminated at each carbide particles. These curves show dislocation-like contrast in TEM bright field images. Impurity elements are probably enriched at such boundaries.

Simply speaking, during the γFe → α-Fe solid-solid transformation, the microstructure (martensite) formed in the quenched sample with low Ms can be treated as an earlier stage of the microstructure formed in the quenched sample with high Ms. The formation mechanism of pearlite and bainite structure can also be considered in this way as explained in Fig. 12.

5. Conclusions
The microstructure in quenched three Fe-xC (x = 0.02, 0.05 and 0.1 wt.%) alloys has been investigated using TEM:

1. Lath martensite structure has been observed in all quenched samples regardless of carbon content.
2. {112}<111>-type twinning structure is a common martensitic substructure in quenched Fe-0.1C samples. The fine α-Fe(c) particles are located at the twinning boundaries.
3. Lath martensitic structure and the fine θ-Fe2C particles formed in the quenched ultra-low carbon alloys can be explained based on the {112}<111>-type twinning structure with a high density of α-Fe(c) particles at the twinning boundaries.

Acknowledgments
This work was supported by JSPS KAKENHI Grant Number JP15H02304. Thanks are due to Prof. Y. Tomota for helpful discussion and manuscript reading. We would also like to thank Mr. S. Kawada (Materials Analysis Station, NIMS) for the assistance with ICP-OES measurement.

REFERENCES
1) E. C. Bain: Trans. AIME, 70 (1924), 25.
2) W. L. Fink and E. D. Campbell: Trans. Am. Soc. Steel Treat., 9 (1926), 717.
4) C. S. Roberts: Trans. AIME, 197 (1953), 203.