Precipitation of paraequilibrium cementite: Experiments, and thermodynamic and kinetic modeling

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Abstract

The precipitation of cementite prior to the precipitation of the strengthening $\text{M}_{2}\text{C}$ phase is investigated using two model ultra-high strength (UHS) steels. The structure, microstructure and chemical composition of cementite are studied by analytical electron microscopy techniques. The structure of cementite precipitated during early stages of tempering at 755 and 783 K was confirmed by convergent beam electron diffraction. In an alloy containing 0.16 mass% C, the cementite particles were primarily plate shaped and interlath type, whereas in an alloy containing 0.247 mass% C both inter- and intralath particles were observed. Consistent with the earlier studies on tempering of Fe-C martensite, lattice imaging of cementite suggests microsyntactic intergrowth of $\text{M}_{2}\text{C}_{3}$ (Haggb carbide). Quantification of the substitutional elements in cementite confirms its paraequilibrium state with ferrite at the very early stage of tempering. Computational thermodynamic and kinetic tools, Thermo-Calc and DICTRA (diffusion controlled transformation) software, respectively, are used to model the precipitation of paraequilibrium cementite in several multicomponent alloys. A thermodynamic model parameter describing the effect of Si on the stability of cementite is proposed. The model parameter is consistent with the following results: (a) that Si does not partition to cementite in Fe–Si–C and Co–Si–C alloys under orthoequilibrium conditions, and (b) there is a large driving force for the precipitation of paraequilibrium cementite in an Fe–0.41C–3Mn–2Si alloy where it has been experimentally verified. The nucleation driving forces for the precipitation of paraequilibrium cementite, and the two-phase (ferrite and cementite) paraequilibrium boundaries for multicomponent alloys are calculated using the Thermo–Calc software systems. The results of growth simulations of cementite under paraequilibrium condition in multicomponent systems using the DICTRA software are also presented. © 2002 Acta Materialia Inc. Published by Elsevier Science Ltd. All rights reserved.

Keywords: Analytical electron microscopy; Cementite; Thermodynamics; Kinetics

1. Introduction

The quantitative predictions of processing-microstructure-properties links in modern ultra-

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the alloy composition, there can be a significant overlap in the kinetics of these three precipitation processes. A science-based alloy design approach [1] requires that the necessary models and tools be developed to control the dynamics of microstructural evolution. Of particular importance in the case of UHS steels is the precipitation of cementite and its thermodynamic and kinetic status while the precipitation secondary hardening, coherent M$_{2}$C takes place.

The kinetic theories of diffusional phase transformations in alloys containing both substitutional and interstitial elements are well developed [2–8]. An important feature of various kinetic models is the assumption of local equilibrium at the interface. Depending on the interface velocity during transformation, it is convenient to classify the kinetics into two distinct modes:

1. partitioning local equilibrium is characterized by low interface velocity while maintaining local equilibrium at the interface. This condition is also referred to as orthoequilibrium (OE). The overall kinetics of OE transformation is governed by the slowest diffusing species (substitutional element). The thermodynamic condition for OE between ferrite (α) and cementite (θ) in steels is given by

\[
\mu_\alpha^\alpha = \mu_\theta^\theta
\]  
(1)

where \(\mu_i\) is the chemical potential of element \(i\) (=C, Co, Cr, Fe, Mn, Mo, Ni, Si).

2. paraequilibrium (PE) is a kinetically constrained equilibrium when the diffusivity of the substitutional species is negligible compared to that of interstitial species. The kinetics of PE is governed by the fastest diffusing species, which is either C or N in steels. Hultgren [2] argued that if carbon diffuses appreciably faster than the substitutional alloying elements, then the growing phase inherits the substitutional alloy contents. Furthermore, if the substitutional alloying elements are not allowed to partition, their individual chemical potentials have no physical relevance and thus the thermodynamic behavior of these elements can be expressed by one hypothetical element, \(Z\). Then, PE is defined by a uniform carbon potential and a uniform site fraction of substitutional elements across the transforming interface. For example, in the case of α/θ transformation, the thermodynamic conditions for PE are given by

\[
\mu_\alpha^\alpha = \mu_\theta^\theta
\]  
(2a)

\[
y_j^\alpha = y_j^\theta
\]  
(2b)

\[
\mu_j^\alpha = \sum y_j^\alpha \mu_j^\alpha = \mu_j^\theta = \sum y_j^\theta \mu_j^\theta
\]  
(2c)

where \(y_j\) are the site fractions of substitutional element \(j\) (=Co, Cr, Fe, Mn, Mo, Ni, Si). For a system containing both substitutional (\(j\)) and interstitial element (\(C\)), the site fractions are related to the ordinary mole fractions (\(x\))

\[
y_j = \frac{x_j}{1-x_C}
\]  
(3a)

\[
y_C = \frac{p}{q} \frac{x_C}{1-x_C}
\]  
(3b)

According to a two sublattice model [9] used here to express the Gibbs energies, \(p=1\) and \(q=3\) for ferrite, and \(p=q=1\) for austenite.

The schematic concentration profiles across the transforming interface for the above two distinct modes are shown in Fig. 1. The PE growth mode can also be conceived as the complete solute trapping [10] in the substitutional sublattice. The cen-

![Schematic profiles of the site fractions of the substitutional elements (y_j) and C (y_C) across the transforming interface associated with (a) OE and (b) PE phase transformation involving ferrite (α) and cementite (θ). The X-axis represents distance and the Y-axis represents concentration. The cementite is the growing phase.](image-url)
The central idea behind solute trapping is that when the interface velocity is greater than the diffusional velocity, the solute atoms will be trapped behind the advancing interface. The extent of solute trapping is determined by the magnitude of the interface velocity, relative to the diffusional velocity. The former should be much greater than the latter for complete solute trapping. An intermediate case (incomplete solute trapping) between OE and PE is often referred to as no-partition local equilibrium (NPLE).

The tracer diffusivities \( (D_{T}) \) of C [11], Co [12], Cr [13], Mn [14], Mo [15], and Ni [12] in pure α-Fe in the temperature range of tempering experiments, 600–800 K, are listed in Table 1. It is seen that the substitutional elements diffuse about 8–13 orders of magnitude slower than carbon. Under such conditions the early stages of transformation kinetics is expected to be controlled by the diffusion of C alone when the substitutional atoms may be considered to be configurationally frozen in both parent and product lattice sites. An excellent example is the precipitation of cementite during bainitic transformation or tempering of martensite.

The composition of cementite with respect to substitutional elements in bainitic or tempered martensite has been investigated many times. Baker and Nutting [16] used the energy dispersive X-ray (EDX) analysis of cementite particles in extraction replica and showed that the substitutional solute content in cementite after short tempering times at 673 and 773 K in an Fe-0.15C-2.25Cr-1Mo steel was similar to that of bulk alloy composition. Chance and Ridley [17] investigated the chromium partitioning of cementite in a bainitic microstructure formed at 823 K in an Fe-0.8C-1.41Cr steel using EDX analysis of extraction replicas. They found very little evidence for chromium partitioning. Babu et al. [18,19] used the atom probe field-ion microscopy (APFIM) technique to study the composition of cementite that formed during tempering of an Fe-0.41C-3Mn-2Si steel in the temperature range of 623–773 K. Their results showed that the substitutional alloy content in cementite was the same as that in the starting alloy at an early stage of tempering; thus, confirming cementite growth by the PE mode. This is despite the fact that equilibrium solubility of Si in cementite is practically zero. Furthermore, they did not observe any compositional spike at the cementite/martensite interface, and found that the PE state of cementite moves toward the NPLE state with continued tempering. Thomson and Bhatia [20,21] investigated the chemistry of cementite in an Fe-0.15C-2.25Cr-1Mo steel in the temperature range of 783–893 K and for up to 2072 h of tempering. They used the energy dispersive X-ray (EDX) analysis of cementite particles in extraction replicas and found that the Cr-content of cementite slowly evolves from somewhat closer to the paraequilibrium value than to the orthoequilibrium value. Thomson and Miller [22–24] also used the APFIM technique and studied the composition of cementite in an autotempered Fe-0.1C-3Mn steel, and also in Fe-0.15C-2.25Cr-1Mo and Fe-0.4C-2.25Cr-1Mo steels after tempering for various times at 623 and 723 K. In all cases, they also did not observe any evidence of partitioning of the alloying elements between cementite and martensite, nor did they observe any compositional spike at the cementite/martensite interface. Very recently, Ghosh et al. [25] reported the compo-

<table>
<thead>
<tr>
<th>Element</th>
<th>( D_T ) at 600 K, m(^2)/s</th>
<th>( D_{T}/D_T^a ) at 600 K</th>
<th>( D_T ) at 800 K, m(^2)/s</th>
<th>( D_{T}/D_T^a ) at 800 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>9.466×10^-12</td>
<td>1.626×10^-13</td>
<td>6.418×10^-13</td>
<td>1.115×10^{-11}</td>
</tr>
<tr>
<td>Co</td>
<td>1.399×10^-26</td>
<td>1.319×10^-12</td>
<td>7.154×10^-23</td>
<td>5.594×10^-10</td>
</tr>
<tr>
<td>Cr</td>
<td>1.399×10^-25</td>
<td>8.867×10^-13</td>
<td>1.270×10^-20</td>
<td>1.979×10^{-19}</td>
</tr>
<tr>
<td>Mo</td>
<td>8.294×10^-26</td>
<td>8.867×10^-13</td>
<td>8.34×10^-20</td>
<td>1.298×10^{-19}</td>
</tr>
<tr>
<td>Mn</td>
<td>6.867×10^-28</td>
<td>7.254×10^-12</td>
<td>8.34×10^-20</td>
<td>1.298×10^{-19}</td>
</tr>
<tr>
<td>Ni</td>
<td>5.593×10^-26</td>
<td>5.909×10^-13</td>
<td>1.25×10^-20</td>
<td>1.949×10^{-19}</td>
</tr>
</tbody>
</table>
sition of cementite that formed during tempering of an Fe–0.247C–16.08Co–0.71Cr–2.28Mo–4.97Ni alloy at 783 K for up to 15 min. They carried out high-resolution EDX analysis of the extracted particles in an AEM, and found that the substitutional alloy content in cementite was the same as that in the starting alloy, thus, confirming the PE nature of the precipitated cementite.

Here, we report the results of cementite precipitation in two model UHS steels using analytical electron microscopy (AEM) techniques. The composition of cementite is determined for up to 1 h of tempering. As a part of our ongoing research it has been realized that to quantify and to model the secondary hardening process, it is necessary to ascertain the thermodynamic and kinetic status of cementite. This is because the precipitation of cementite very strongly influences the C content of the ferrite matrix which in turn determines the driving force and the dynamics of M$_2$C precipitation giving rise to secondary hardening. We also model the thermodynamic and kinetic aspects of cementite precipitation in multicomponent alloys using the Thermo-Calc [26] and dictra [27] software systems.

2. Materials and experimental procedures

Two model alloys, C3B and 1605-2C, were used for experimental investigation of the structure, microstructure and composition of the cementite that forms prior to the precipitation of M$_2$C phase. The C3B is a prototype secondary-hardening carburizing steel [28]. The 1605-2C steel is an experimental alloy employed in previous fundamental studies of M$_2$C secondary hardening behavior [29]. The composition of these model alloys along with two power plant steels and two low alloy steels in which the precipitation of cementite have recently been studied are listed in Table 2. All six alloys are used for thermodynamic and kinetic modeling.

The C3B was solution treated at 1273 K for 1 h and 1605-2C was solution treated at 1398 K for 1.5 h, both in an inert argon environment. Solution treatment was followed by an oil quench to room temperature. Tempering experiments were performed in a molten salt bath. The C3B was tempered at 755 K in for 5, 10, 15, 30, and 60 min, and the 1605-2C was tempered at 783 K in for 5, 10, and 15 min. After tempering the samples were water quenched to room temperature.

Extraction replicas of heat treated materials were prepared by depositing a thin carbon film on a polished and etched surface. The carbon film was then floated off the specimens in a solution of 5% nitric acid in methanol and collected on palladium-coated copper grids. The extraction replicas were examined in the AEM to determine the structure by convergent beam electron diffraction (CBED) and to determine the composition by energy dispersive X-ray (EDX) microanalysis.

Conventional transmission electron microscopy (TEM) was carried out in a Hitachi 8100 microscope operating at 200 kV. The high-resolution electron microscopy (HREM) and analytical characterization were performed in a cold field emission gun high resolution AEM (Hitachi HF-2000) equipped with a Gatan 666 parallel electron energy loss spectrometry (PEELS) detector, an ultrathin window (ATW) Link EDX detector and data processor (QX2000) and a Gatan CCD camera for HREM imaging. The AEM was operated at 200 kV. The take-off angle for the X-ray detector was 68°. The X-ray collection time was 100 s and the electron probe size was about 8 nm. Care was taken to insure that the particle being analyzed was not in a two-beam condition in order to minimize electron-channeling effects [30]. The X-ray spectra was deconvoluted, to separate the overlapping peaks, and the background subtracted integrated intensities were obtained using the Desktop Spectrum Analyzer (DTSA 2.5.1) software [31].

Fig. 2 shows a typical EDX spectrum from a plate shaped cementite particle in C3B after 15 min of tempering at 755 K. The background subtracted integrated intensities of such spectra were converted to compositions by using the following Eqs. [30]

$$ w_j = k_j \rho_j \frac{I_j}{I_{Fe}} \left[ \frac{1}{I_{Fe}} \right] \left( \frac{1 + \rho_j}{I_{Fe}} \right) $$

$$ w_{Co} + w_{Cr} + w_{Fe} + w_{Mo} + w_{Ni} = 1 $$

where $j$=Co, Cr, Ni, and Mo, $w_j$ is the weight frac-
Table 2
Composition (in wt.%) of model ultrahigh strength (UHS) steels, power plant steels and low-alloy steels used in this study (only the first two alloys are used for experimental investigation while all are used for thermodynamic and kinetic modeling)

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Fe</th>
<th>C</th>
<th>Co</th>
<th>Cr</th>
<th>Mo</th>
<th>Mn</th>
<th>Ni</th>
<th>Si</th>
<th>V</th>
</tr>
</thead>
<tbody>
<tr>
<td>C3B</td>
<td>balance</td>
<td>0.16</td>
<td>28.00</td>
<td>5.10</td>
<td>2.50</td>
<td>–</td>
<td>3.00</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>1605-2C</td>
<td>balance</td>
<td>0.24</td>
<td>16.08</td>
<td>0.71</td>
<td>2.28</td>
<td>–</td>
<td>4.97</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>FeCrMoC*</td>
<td>balance</td>
<td>0.15</td>
<td>–</td>
<td>2.25</td>
<td>1.00</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>FeCrMoC2k</td>
<td>balance</td>
<td>0.40</td>
<td>–</td>
<td>2.25</td>
<td>1.00</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>FeMnC*</td>
<td>balance</td>
<td>0.10</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>3.13</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>FeMnSiC</td>
<td>balance</td>
<td>0.41</td>
<td>–</td>
<td>–</td>
<td>3.00</td>
<td>2.00</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

* Reference [22,24].

Fig. 2. An as-collected EDS X-ray spectrum from a plate shaped cementite particle after tempering C3B at 755 K for 15 min. The X-ray collection time was 100 s. Background subtracted integrated intensities were obtained by deconvoluting the peaks using DTA software [31].

The 

\[ \frac{k_{Fe}}{\text{primary}} \] 

factors were determine using thin foils of two fully solution treated alloys: C3B and 1605-2C. The X-ray spectra were collected from foil thicknesses of 100 nm or less. The foil thickness was determined by CBED [36]. For both standards, in the above thickness ranges Co, Cr, and Ni satisfied the criteria of a thin foil while the ACF correction for Mo was about 5%. Among the elements of interest, Cr-Kα can be fluoresced by Fe-Kα, which in turn can be fluoresced by Ni-Kα. The fluorescence yield due to Kβ radiation was neglected. For both standards the fluorescence yields were found to be negligible.

The statistical accuracy of the composition determination from Eq. (4) is primarily limited by the counting statistics of the X-ray collection process [31,37]. When the X-ray spectra are collected for a sufficiently long time to obtain several thousand counts in each peak, the counting statistics can be assumed to follow a normal distribution. However, in a multicomponent system it may be difficult to satisfy this criterion for each element if experiments are to be carried out within a reasonable period of time. Nevertheless, since the composition of cementite was determined by analyzing about 30 different particles, the confidence interval is estimated by the statistics of the student t-distribution. The total relative error (\( \Delta c_{ej} \)) in the determination of composition is given by

\[ \Delta c_{ej} = \Delta c_{Fe} + \Delta c_{Fe/Fe} \]
where $\Delta e_{\text{ag}}$ and $\Delta e_{\text{igg}}$ are the relative errors associated with k-factors and in the counting statistics of X-rays in the specimen of unknown composition, respectively. They are given by [37]

$$\Delta e_{\text{ag}} = \frac{100}{n} \frac{\bar{e}_{\text{ag}}}{\text{ag}}$$

(7)

$$\Delta e_{\text{igg}} = \frac{100}{n} \frac{\bar{e}_{\text{igg}}}{\text{igg}}$$

(8)

where $t_{0.99}$ are the student t values for n measurements at 99% confidence level, $\sigma_k$ and $\sigma_{\text{igg}}$ are the standard deviations for k-factor and intensity ratio measurements, respectively, $\bar{e}_{\text{ag}}$ is the mean of n values of k-factor, and $I/I_{\text{igg}}$ is the mean of n values of $I/\text{igg}$. Since the concentrations of only substitutional elements were determined, their site fractions in the metal sublattice are given by the respective atomic fractions.

3. Experimental results

3.1. Microstructure and structure of precipitated cementite

Fig. 3(a) shows the bright-field TEM micrograph of lath martensite in C3B. It is seen that there is a distribution of the width of the laths, and we believe this is due to the geometric partitioning of the prior austenite grain. While the first formed laths are about 0.5 \( \mu \)m wide, those formed at the last stages of transformation (shown with arrows) are only 10–20 nm wide. Fig. 3(b) shows the bright-field TEM micrograph of C3B tempered at 755 K for 15 min. The presence of plate shaped cementite particles (marked with arrows) amidst a high density of dislocations may be noted.

An unambiguous interpretation of the nature of ferrite-cementite equilibrium can be made if the composition analysis of cementite (product phase) in AEM is not affected by the presence of a ferrite (parent phase) matrix. Quantitative X-ray microanalysis in thin foils requires that the precipitate extend through the thickness of the foil. Otherwise, the collected X-ray spectrum may contain contributions from both the precipitate and matrix phases and the determination of the exact composition of the precipitate becomes difficult. Therefore, to avoid these uncertainties we have chosen to use extraction replicas only for determining the composition. Besides eliminating the effect of the matrix, the extraction replica technique is very convenient for relatively rapid composition analysis and collecting statistically significant data. These factors are important in this study due to the highly dislocated martensitic substructure and heterogeneous nature of cementite precipitation.
which make their identification and chemical analysis more time consuming if thin foil specimens are used.

The structure of cementite is well established [38-40]. It has an orthorhombic structure with space group \( \text{Pnma} \) (no. 62). The atom positions are given by \( C (x=0.89, y=0.25, z=0.45) \) at 4c, \( \text{Fe} (x=0.186, y=0.063, z=0.328) \) at 8d and \( \text{Fe}_2 \) 
\( (x=0.036, y=0.25, z=0.852) \) at 4c. The lattice parameters are \( a=0.509 \text{nm}, b=0.6748 \text{nm}, c=0.4523 \text{nm} \) [40]. To confirm the structure of the extracted particles in our alloys, CBED patterns were recorded from several. Fig. 4(a)–(c) show the CBED patterns of cementite along \([001]_{Z_{\text{A}}}, [013]_{Z_{\text{A}}}, [113]_{Z_{\text{A}}} \), respectively. These are consistent with the known structure of cementite. The kinetically forbidden \((h00)\) and \((hh0)\) reflections with \( h=(2k+1), \quad k=0,1,2,\ldots \) in Fig. 4(a)–(c) are attributed to double diffraction effects. These reflections are shown with arrows.

Fig. 5(a)–(d) show the bright-field TEM micrographs of the cementite particles, formed in C3B after tempering at 755 K, in extraction replicas. The cementite particles are primarily plate shaped and interlath type. Fig. 6 shows an enlarged view of a plate shaped cementite having an edge-on orientation. Typically the cementite particles in C3B have a diameter of about 150 nm and thickness of about 20 nm. Fig. 7(a) and (b) show bright-field TEM micrographs of the cementite particles, formed in 1605-2C after tempering at 788 K, in extraction replicas. Unlike C3B, the cementite particles in 1605-2C may be categorized as intra- and interlath types. It is believed that both intra- and interlath cementite particles nucleate heterogeneously, the former in the vicinity of dislocations within the martensite lath and the latter in the martensite lath boundaries. The interlath particles are somewhat irregular in shape. Generally, the intralath cementite particles are smaller than the interlath cementite particles.

The structural changes taking place during tempering are classified into three stages. The stage I corresponds to the precipitation of carbide (around 370 K, 1 h). The stage II corresponds to the decomposition of austenite (around 550 K, 1 h). The stage III corresponds to the precipitation of cementite (between 550 and 800 K, 1 h). The tempering temperature in this study falls in the last range. Even though the final product after stage III tempering is cementite \((\text{Fe},\text{C})\), a question remains if the Hägg carbide \((\text{Fe}_2\text{C}_2)\) appears at the early stage of stage III tempering [41-43].

Fig. 8 shows a lattice image, taken close to \([210]_{Z_{\text{A}}} \), of plate shaped cementite formed in 1605-2C after 5 min of tempering at 783 K. Many planar defects parallel and perpendicular to the lattice fringes may be observed. The latter (shown with white arrows) are likely the growth defects due to end-on collision of the platelets which are typically 3–5 nm thick. Fig. 8 suggests that the platelets nucleate independently, but have the same orientation relationship with the matrix. Their rapid radial growth causes end-on coalescence. The other major type of planar defect regions are about 1 nm thick. These regions are most likely due to the microsyntactic intergrowth of the \( \text{Fe}_2\text{C}_2 \) Hägg carbide. The stacking mode of cementite can be described by two kinds of prism layers, A and B, which are rotated by 180° with respect to each other about the normal of the prism layer [44]. The stacking sequence of cementite is \( \text{A}/\text{B}/\text{A}/\text{B}/\ldots \) with a stacking period of 0.34 nm. The structure of \( \text{Fe}_2\text{C}_2 \) can be derived from double prism layers where two kinds of prism layers are linked together by sharing the prism edges. Thus the stacking sequence of \( \text{Fe}_2\text{C}_2 \) can be expressed as \( \text{AB}/\text{AB}/\text{AB}/\ldots \). The structure of higher order carbides (general formula \( \text{Fe}_{2+1t}\text{C}_t \) and \( t>1 \)) differs from cementite only in the number of linked prism layers. Thus, they can grow along an axis normal to the stacking plane giving rise to microsyntactic intergrowth. Depending on the tempering temperature, microsyntactic growth of several higher order carbides within cementite is possible. However, it is believed that above about 673 K only \( \text{Fe}_2\text{C}_2 \) intergrows within cementite [45]. Fig. 8 also suggests the presence of stacking disorder within the cementite regions. All these observations are consistent with the faulted cementite structure reported earlier [44]. Even though cementite is more stable than Hägg carbide, the microsyntactic intergrowth of the latter may be promoted by interfacial matching, similar to the role of stacking faults in carbide plates [46]. The tempering studies of Fe-C martensite by Nagakura et al. [44–45] indicate that
Fig. 4. Convergent beam electron diffraction patterns of cementite formed in C3B at 755 K: (a) [001] zone axis (b) [013] zone axis, and (c) [113] zone axis.

the frequency and extent of microsyntactic intergrowth of Hägg carbide in cementite is a function of aging temperature. This is consistent with our observation of fewer and thinner intergrowth regions compared to those reported by Nagakura et al.

3.2. Composition of precipitated cementite

The $k$-factors needed to quantify the composition of cementite were determined using thin foils of solution treated and quenched specimens. These were determined to be $k_{\text{C_MF}} = 1.0629 \pm 0.0096$. 
Fig. 5. Bright-field TEM micrographs (extraction replica) of C3B showing cementite particles after tempering at 755 K: (a) 5 min, (b) 10 min, (c) 30 min, and (d) 60 min.

Fig. 6. Bright-field TEM micrograph (extraction replica) of C3B showing a cementite particle formed during tempering at 755 K for 15 min. The plate shaped particle with edge-on orientation exhibits its two principal dimensions.
each cementite particle analyzed was not determined. However, the thickness of a few of the large particles analyzed was found to lie in the range 50–60 nm. In this thickness range the ACF for Mo is about 2%. The fluorescence yields for Cr–Kα and Fe–Kα were negligible. Fig. 9 shows the distribution of concentrations of Co, Cr, Mo, and Ni in cementite, after 5 min of tempering of C3B at 755 K, as a function of Fe–Kα counts. For each heat treatment, about 30 cementite particles were randomly selected and the X-ray spectra were collected. Even though many of these data represent cementite particles having different thickness, it is important to bear in mind that in a cold field emission microscope, higher count does not necessarily imply higher thickness of the specimen being analyzed. The measured metal site fractions of the various constituents as a function of tempering time of C3B and 1605-2C are listed in Tables 3 and 4, respectively. An error bar at 99% confidence level for all measured quantities are also given. As one would expect, the major source of relative error of the measured quantities is due to the counting statistics i.e., Eq. (8). It accounts for more than 50% of the total relative error.

The initial site fractions of Co, Cr, Fe, Mo, and Ni in the matrix C3B are 0.2719, 0.0561, 0.6277, 0.0149, and 0.0293, respectively. At the shortest tempering time of 5 min, among the substitutional alloying elements Cr exhibits maximum deviation from the corresponding paraequilibrium value. The temporal evolution of the site fractions of Co, Cr, Mo and Ni are shown in Fig. 10. With continued tempering, the site fractions of Cr and Mo increase while that of Co decreases. The site fraction of Ni remains virtually unchanged up to 60 min. While the temporal evolution of Co and Ni contents is consistent with the expected trend for the transition from paraequilibrium towards orthoequilibrium state, Mo does not exhibit this trend. This suggests the possibility of intermediate thermodynamic states due to the multicomponent nature of the system. The initial site fractions of Co, Cr, Fe, Mo, and Ni in the matrix of 1605-2C are 0.1562, 0.0078, 0.0168, and 0.0485, respectively. As seen in Table 4, these values are in good agreement with the measured average compositions after 5 and 10 min of tempering.

During X-ray spectra collection the thickness of
Fig. 8. Lattice image of a plate shaped cementite particle in 1605-2C, formed after 5 min of tempering at 783 K, showing numerous planar defects. The defects perpendicular to the lattice fringes (shown with white arrows) are due to an end-on coalescence of the platelets and the defects parallel to the lattice fringes (shown with dark arrows) are most likely due to mesosynthetic intergrowth of HAGG carbide (Fe$_2$C$_3$ or M$_2$C$_3$).

![Image](image)

Fig. 9. The distribution of concentrations (in wt. Fe) of Co, Cr, Mo, and Ni in PE-$\theta$, as a function of integrated intensity of Fe, after tempering alloy C3B for 5 min at 755 K. Horizontal lines indicate the average composition.

4. Thermodynamic and kinetic modeling

4.1. Thermodynamic modeling of the paraequilibrium cementite precipitation

In an earlier paper [47] we had described the implementation of paraequilibrium thermodynamics in conjunction with the SSOL database [48] of Thermo-Calc software systems. Since the substitutional alloying elements are not allowed to partition during PE-$\alpha$/PE-$\theta$ transformation, we define a hypothetical element $Z$ whose thermodynamic properties in the phase $\psi$ are expressed in terms of the thermodynamic properties of the real elements in that phase.

The Thermo-Calc software employs the sublattice model [49] to express the Gibbs energies of phases in multicomponent systems. Besides the excess Gibbs energies of mixing, the model also accounts for the Gibbs energy contributions due to magnetic and atomic ordering. For a multicomponent ferrite phase ($\alpha$), the sublattice representation is $(x_{1},x_{2},x_{3},...,)(C,Va)$_{y}$, where $x_{i}$s are the substitutional elements, C and Va are carbon and the interstitial vacancy. Then, the molar Gibbs energy of $\alpha$ is given by

$$G_{m}^{\alpha} = y_{C}\sum x_{i}G_{i}^{\theta} + y_{Va}\sum x_{i}G_{i}^{Va}$$

$$+ RT(\sum x_{i}\ln x_{i} + \sum x_{i}y_{C}\ln y_{C} + \sum x_{i}y_{Va}\ln y_{Va})$$

$$+ G_{m}^{\alpha\psi} + G_{m}^{\text{mix,}\alpha}$$

where $y_{i}$s are the site fractions of the element $j$, $y_{C}$ and $y_{Va}$ are the site fractions of carbon and vacancy. The parameters $G_{i}^{\theta}$ and $G_{i}^{Va}$ represent the molar Gibbs energy of the $\alpha$ phase when the first sublattice is fully occupied by the element $j$ and the second sublattice is fully occupied by either C or Va, respectively. In Eq. (9), the first two terms
Table 3
The calculated metal site fractions in cementite in the orthoequilibrium and paraequilibrium states with ferrie are compared with those measured after 5, 10, 15, 30 and 60 min of tempering the C3B at 755 K.

<table>
<thead>
<tr>
<th></th>
<th>Co</th>
<th>Cr</th>
<th>Fe</th>
<th>Mo</th>
<th>Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>Orthoequilibrium (Eq. (1))</td>
<td>0.0046</td>
<td>0.9775</td>
<td>0.0151</td>
<td>0.0019</td>
<td>0.0009</td>
</tr>
<tr>
<td>Paraequilibrium (Eq. (2))</td>
<td>0.2719</td>
<td>0.0561</td>
<td>0.6277</td>
<td>0.0149</td>
<td>0.0293</td>
</tr>
<tr>
<td>Measured after 5 min at 755 K</td>
<td>0.2763 (0.2840±0.0077)</td>
<td>0.0748 (0.0678±0.0055)</td>
<td>0.5985 (0.5828)</td>
<td>0.0209 (0.0349±0.0067)</td>
<td>0.0296 (0.0303±0.00270)</td>
</tr>
<tr>
<td>10 min at 755 K</td>
<td>0.2710</td>
<td>0.0790</td>
<td>0.6011</td>
<td>0.0194</td>
<td>0.0295</td>
</tr>
<tr>
<td>15 min at 755 K</td>
<td>0.2629</td>
<td>0.0802</td>
<td>0.6052</td>
<td>0.0191</td>
<td>0.0291</td>
</tr>
<tr>
<td>30 min at 755 K</td>
<td>0.2635 (0.2702±0.0073)</td>
<td>0.0707 (0.0727±0.0059)</td>
<td>0.5900 (0.5864)</td>
<td>0.0193 (0.0325±0.0112)</td>
<td>0.0302 (0.0302±0.0037)</td>
</tr>
<tr>
<td>60 min at 755 K</td>
<td>0.2532 (0.2707±0.0094)</td>
<td>0.0771 (0.0771±0.0093)</td>
<td>0.5793 (0.5793)</td>
<td>0.0193 (0.0391±0.0103)</td>
<td>0.0328 (0.0317±0.0053)</td>
</tr>
</tbody>
</table>

* The uncertainties correspond to the total error (Eq. (6)) at 99% confidence level.
* The metal site fractions in the starting alloy are y_{Co}=0.2719, y_{Cr}=0.0561, y_{Fe}=0.6277, y_{Mo}=0.0149, and y_{Ni}=0.0293.
* The measured weight fractions of the metal constituents in cementite are shown in parenthesis.

Table 4
The calculated metal site fractions in cementite in the orthoequilibrium and paraequilibrium states with ferrie are compared with those measured after 5, 10, and 15 min of tempering the 1605-2C at 788 K.

<table>
<thead>
<tr>
<th></th>
<th>Co</th>
<th>Cr</th>
<th>Fe</th>
<th>Mo</th>
<th>Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>Orthoequilibrium (Eq. (1))</td>
<td>0.0324</td>
<td>0.1912</td>
<td>0.6131</td>
<td>0.1403</td>
<td>0.0229</td>
</tr>
<tr>
<td>Paraequilibrium (Eq. (2))</td>
<td>0.1562</td>
<td>0.0078</td>
<td>0.7707</td>
<td>0.0168</td>
<td>0.0485</td>
</tr>
<tr>
<td>Measured after 5 min at 783 K</td>
<td>0.1523 (0.1571±0.0092)</td>
<td>0.0093 (0.0085±0.0010)</td>
<td>0.7725 (0.7551)</td>
<td>0.0177 (0.0297±0.0066)</td>
<td>0.0395 (0.0395±0.0044)</td>
</tr>
<tr>
<td>10 min at 783 K</td>
<td>0.1523</td>
<td>0.0083</td>
<td>0.7751</td>
<td>0.0176</td>
<td>0.0466</td>
</tr>
<tr>
<td>15 min at 783 K</td>
<td>0.1412 (0.1455±0.0064)</td>
<td>0.0116 (0.0076±0.0014)</td>
<td>0.7578 (0.7578)</td>
<td>0.0156 (0.0296±0.0061)</td>
<td>0.0479 (0.0479±0.0047)</td>
</tr>
</tbody>
</table>

* The metal site fractions in the starting alloy are y_{Co}=0.1562, y_{Cr}=0.0078, y_{Fe}=0.7707, y_{Mo}=0.0168, and y_{Ni}=0.0485. 
* The uncertainties correspond to the total error (Eq. (9)) at 99% confidence level.
* The measured weight fractions of the metal constituents in cementite are shown in parenthesis.

correspond to the Gibbs energies due to mechanical mixture, the third term is the ideal Gibbs energy of mixing, the fourth term is the excess Gibbs energy of mixing which is expressed as a Redlich–Kister–Muggiani polynomial [50], and the fifth term is the Gibbs energy contribution due to magnetic ordering, A is the universal gas constant, and T is the absolute temperature. According
Fig. 10. Temporal evolution of the site fractions of Co, Cr, Mo, and Ni in PE-θ of C3B tempered at 755 K. Horizontal lines indicate the site fractions corresponding to paraequilibrium conditions.

to the model proposed by Hillert and Jarl [51], the quantity $G_{m\text{mag,}\alpha}^{\text{para}}$ in Eq. (9) is expressed as

$$G_{m\text{mag,}\alpha}^{\text{para,}\alpha} = RT\ln(\beta^\alpha + 1)/\tau^\alpha$$

(10)

where $\beta^\alpha$ is the average magnetic moment in Bohr magnetons of $\alpha$ and $\tau^\alpha = T/T_c^\alpha$ with $T_c^\alpha$ being the Curie temperature of $\alpha$. The function $f(\tau^\alpha)$ is expressed as truncated polynomials [51]. Like the excess thermodynamic properties, the composition dependence of $\beta^\alpha$ and $T_c^\alpha$ in a multicomponent system are also expressed by Redlich–Kister polynomials.

Under paraequilibrium conditions, the sublattice description for the $\alpha$ phase (PE-α) is $(Z)(C,\text{Va})_3$ where $Z$ is a hypothetical element. Then, the molar Gibbs energy of PE-α is expressed as

$$G_{m\text{mag,PE-}\alpha}^{\text{PE-}\alpha} = y_C G_{Z\text{C}}^{\text{PE-}\alpha} + y_{\text{Va}} G_{Z\text{Va}}^{\text{PE-}\alpha} + RT(3y_C\ln y_C + 3y_{\text{Va}}\ln y_{\text{Va}}) + G_{m\text{mag,PE-}\alpha}$$

(11)

$$G_{m\text{mag,PE-}\alpha}^{\text{PE-}\alpha} = RT\ln(\beta^{\text{PE-}\alpha} + 1)/\tau^{\text{PE-}\alpha}$$

(12)

where $\beta^{\text{PE-}\alpha}$ is the average Bohr magneton of PE-α and $\tau^{\text{PE-}\alpha} = T/T_c^{\text{PE-}\alpha}$ with $T_c^{\text{PE-}\alpha}$ being the Curie temperature of PE-α. In an earlier paper [47], we had demonstrated the one-to-one correspondence between the parameters in Eqs. (9) and (10) vis-à-vis Eqs. (11) and (12). In other words, all thermodynamic parameters including the composition dependence of Bohr magneton moment and Curie temperature of PE-α can be very easily calculated from those of the $\alpha$ phase. However, it is not necessary that these cumbersome calculations be performed manually on a case by case basis. Rather, for any given multicomponent system it is possible to rewrite the thermodynamic data file of the $\alpha$ phase in such a manner that for any given composition all parameters describing $G_{m\text{mag,}\alpha}^{\text{para,}\alpha}$, $\beta^{\text{PE-}\alpha}$, $T_c^{\text{PE-}\alpha}$ will be automatically calculated by the Thermo-Calc software by knowing only the site fraction of the substitutional elements in that system. In an analogous manner the molar Gibbs energy of paraequilibrium cementite (PE-θ) can also be expressed in terms of the thermodynamic quantities of the cementite phase provided in the SSOL database of the Thermo-Calc software system.

The thermodynamic driving force is a very fundamental quantity in understanding any phase transformation kinetics and mechanism. Using Eq. (11) for PE-α and an analogous equation for PE-θ, we can construct their molar Gibbs energy curves as a function of carbon content. Then, the driving force for nucleation of PE-θ ($\Delta G_{S\text{PE-}\theta}^N$) is given by the parallel tangent construction, as shown schematically in Fig. 11. Then, ($\Delta G_{S\text{PE-}\theta}^N$) is given by

$$-\Delta G_{S\text{PE-}\theta}^N = (\mu_i^{N\text{PE-}\theta} - \mu_i^{N\text{PE-}\alpha}) x_i^{N\text{PE-}\theta}$$

(13)

$$+ (\mu_i^{N\text{PE-}\theta} - \mu_i^{N\text{PE-}\alpha}) x_i^{N\text{PE-}\theta}$$

where $x_i^{N\text{PE-}\theta}$ is the mole fraction of element $i$ in the critical nucleus and $\mu_i^{N\text{PE-}\theta}$ is the corresponding chemical potential. Under orthoequilibrium conditions, the driving force for nucleation is given by

$$-\Delta G_{S\text{PE-}\theta} = (\mu_i^{N\text{PE-}\theta} - \mu_i^{N\text{PE-}\alpha}) x_i^{N\text{PE-}\theta}$$

(14)

where $\mu_i$ ($=\mu_1, \mu_2, ..., \mu_n$) and $x_i$ ($=x_1, x_2, ..., x_n$) are vectors.

To calculate the driving force for nucleation of PE-θ in Si containing alloys, it was necessary to introduce a thermodynamic parameter describing the effect of Si on the stability of cementite,
because such a parameter is currently unavailable in the SSOL database [48]. For the two-sublattice thermodynamic model for cementite used in the SSOL database of the Thermo-Calc software systems, we propose the following parameter (in J/formula unit).

\[
\begin{align*}
G(\text{CEMENTITE}, \text{Si}: \text{C}: 0) & = -H_{298}(\text{GRAPHITE}, \text{C}: 0) \\
& = -3H_{298}(\text{DIAMOND} - \text{A4,SI}: 0) = 250000
\end{align*}
\]  

This parameter was evaluated by a trial and error method utilizing the known phase equilibria of Fe–Si–C and Co–Si–C systems. The reasons for using these two ternary systems as a basis for evaluating the model parameter are: (i) cementite appears in both Fe–C and Co–C phase diagrams, and (ii) the equilibrium phase relationships in these ternary systems are well established. It is well known that the solubility of Si in cementite is practically zero at any temperature under orthoequilibrium condition. We find that the above parameter satisfies this condition for both ternary systems.

The calculated thermodynamic driving forces for the nucleation of PE–θ from fully supersaturated ferrite, in six alloys listed in Table 2, are shown in Fig. 12. In the tempering temperature range of practical interest, 600–800 K, depending on the alloy composition the calculated driving force varies from 3.6 to 10.2 kJ/mol. These driving forces should be considered very high. The elements C, Cr and Mn exert a strong influence in increasing the driving force while Co and Si decreases the driving force for nucleation of PE–θ. As shown in Fig. 12, an important result of the driving force calculation is that even though Si does not partition to cementite under orthoequilibrium condition, there is a fairly large driving force, 3.9–5.9 kJ/mol in the temperature range 623–773 K, for the nucleation of PE–θ from a supersaturated ferrite of Fe–0.41C–3Mn–2Si. This is consistent with the experimental observation of PE–θ in this alloy in the temperature range 623–773 K by Babu et al. [18,19]. In an earlier study [47], we had demonstrated that, among various competing carbides, the driving force for nucleation of PE–θ is the smallest; however, due to the kinetic advantage it forms first during tempering.

Besides calculation of driving force for nucleation under phase equilibrium condition, a further advantage of our approach is that the paraequilibrium phase diagrams of multicomponent sys-
tems can be constructed directly in conjunction with the POLY–8 module of Thermo-Calc software, which are otherwise not possible even in the latest version (v.N). Fig. 13(a) and (b) compare the solubility of C in ferrite under two-phase, ortho- and paraequilibrium conditions as a function of temperature in UHS and low alloy steels. Since paraequilibrium is a constrained equilibrium, at any temperature the solubility of C in ferrite is higher under paraequilibrium compared to the orthoequilibrium condition. This effect is analogous to the effect of misfit strain on the phase equilibria. As shown in Fig. 13, the difference in the solubility of C under OE and PE at any temperature is a strong function of alloy composition.

4.2. Kinetic modeling of the paraequilibrium cementite precipitation

As discussed in Section 3.1, the nucleation of PE–θ is highly heterogeneous. Since we did not measure the heterogeneous nucleation rates of PE–θ at lath boundaries and dislocations, we will not consider the nucleation kinetics. In the following we present the simulation of growth kinetics of PE–θ under paraequilibrium.

To simulate PE growth using the DICTRA [27] software system, we will extend Hultgren’s argument of chemical potentials of substitutional elements under paraequilibrium to include mobility. That is, if the substitutional elements do not partition during a diffusional phase transformation, their individual mobilities have no physical relevance and thus these elements behave kinetically as if there were only one hypothetical element Z. In the following we describe, very briefly, the derivation of the mobilities of C and Z in a multicomponent system.

Thermodynamic factors and the mobilities of the species define the multicomponent diffusion coefficients for each phase. Based on absolute-reaction rate theory arguments, Andersson and Ågren [52] proposed that the mobility of an element i in the phase $\psi(M_T)$ has a frequency factor ($M_{T}^{i\psi}$) and an activation enthalpy factor ($M_{T}^{Q\psi}$), and these are related by the expression

$$M_{T}^{\psi} = \frac{M_{T}^{i\psi}}{RT} \exp\left(-\frac{M_{T}^{Q\psi}}{RT}\right)$$

(16)

Both $M_{T}^{i\psi}$ and $M_{T}^{Q\psi}$ are composition dependent. In the spirit of the CALPHAD approach, Andersson and Ågren [52] proposed that in a multicomponent system both $M_{T}^{i\psi}$ and $M_{T}^{Q\psi}$ be expressed with
a linear combination of the values at each end point of the composition space and a Redlich-Kister-Muggianu polynomial. For the elements and phases of interest in this study, the $M_{i}^{p,\alpha}$ and $M_{i}^{p,\theta}$ parameters were obtained from the mobility database in conjunction with the DICTRA software [53]. From these quantities we can derive the mobilities of C and the hypothetical element $Z$, to simulate PE growth. For example, the mobility of C under paraequilibrium condition can be expressed as

$$\Phi_{C}^{p,\alpha} = y_{C}\Phi_{C}^{p,\alpha}_{C} + y_{Va}\Phi_{Va}^{p,\alpha}_{C}$$

$$= y_{C}\sum_{i \in S} y_{i}\Phi_{i}^{p,\alpha}_{C} + y_{Va}\sum_{i \in S} y_{i}\Phi_{i}^{p,\alpha}_{Va}$$

$$= y_{C}\sum_{i \in S} y_{i}\Phi_{i}^{p,\alpha}_{C} + y_{Va}\sum_{i \in S} y_{i}\Phi_{i}^{p,\alpha}_{Va}$$

(17)

where $\Phi_{i}$ can be either $M_{i}^{p}$ or $M_{i}^{p,\theta}$. In other words, the mobility parameters for C under paraequilibrium condition are the weighted average, with respect to the site fraction of substitutional alloying elements. The quantities $\Phi_{i}^{p,\alpha}_{C}, \Phi_{i}^{p,\alpha}_{Va}$ etc. representing the mobility parameters of C are readily available in the mobility database [53]. Similarly, the mobility of the hypothetical element $Z$ under paraequilibrium condition can be expressed as

$$\Phi_{Z}^{p,\alpha} = y_{C}\Phi_{Z,C}^{p,\alpha} + y_{Va}\Phi_{Va}^{p,\alpha}_{Z,C}$$

$$+ y_{C}y_{Va}\Phi_{Z,C, Va}^{p,\alpha} + y_{C}y_{va}(y_{C} - y_{Va})\Phi_{Z,C, Z}^{p,\alpha}$$

$$= y_{C}\sum_{i \in S} y_{i}\Phi_{i}^{p,\alpha}_{C,Z} + \sum_{j \neq k \neq S} y_{j}\Phi_{j}^{p,\alpha}_{C,Z} + (y_{j}$$

$$- y_{C})\Phi_{j}^{p,\alpha}_{C} + (...)$$

$$+ \sum_{j \neq k \neq S} \sum_{i \in S} y_{i}y_{i}y_{j}\Phi_{i,j}^{p,\alpha}_{C,Z, Va}$$

$$+ y_{Va}\sum_{i \in S} y_{i}\Phi_{i}^{p,\alpha}_{Va,Z} + \sum_{j \neq k \neq S} y_{j}\Phi_{j}^{p,\alpha}_{Va,Z}$$

$$+ (y_{j} - y_{Va})\Phi_{j}^{p,\alpha}_{Va} + (...)$$

$$+ \sum_{j \neq k \neq S} \sum_{i \in S} y_{i}y_{i}y_{j}\Phi_{i,j}^{p,\alpha}_{Va,Z, Va}$$

(18)

$$+ y_{C}y_{Va}(y_{C} - y_{Va})\Phi_{C,Z,Z}^{p,\alpha} + (...)$$

Once again, the mobility parameters for $Z$ can be derived by taking a weighted average of the corresponding parameters with respect to the site fraction of substitutional alloying elements. For the elements of interest here, the parameters $\Phi_{j,k,C}^{p,\alpha}, \Phi_{j,k,C,Z}^{p,\alpha}, \Phi_{j,k,C, Va}^{p,\alpha}, \Phi_{j,k,Va}^{p,\alpha}$ etc. are readily available in the mobility database [53].

Based on the above discussions, it suffices to say that we have rewritten the thermodynamic and the mobility database files for $\alpha$ and $\theta$ phases in a rather generic manner for the Fe–Co–Cr–Mn–Ni–Mo–Si system. Then the simulation of PE–$\theta$ growth for any alloy composition in this system becomes very straightforward by knowing only the site fraction of substitutional alloying elements, and if we restrict ourselves to simple geometries.

We will consider the thickening kinetics of a PE–$\theta$ particle with a flat interface. A simplified representation of an interlath PE–$\theta$ particle is shown in Fig. 14(a) and (b). TEM observation of thin foils reveal that a majority of the laths are about 0.5 $\mu$m thick. From the mass balance criterion alone, the growth of one PE–$\theta$ particle from one martensite lath of 1 $\mu$m wide [Fig. 14(a)] is equivalent to the growth of one PE–$\theta$ particle at the interface of two laths of 0.5 $\mu$m wide each [Fig. 14(b)]. We consider the growth of one interlath PE–$\theta$ particle at the boundary of two martensite laths, which is equivalent to a cell that has a linear dimension of 1 $\mu$m as shown in Fig. 14(a). The governing mass conservation and flux equation under PE condition are

$$\frac{\partial C_{C}}{\partial t} = -\nabla \cdot (J_{C})$$

$$J_{C} = -D_{C} \frac{\partial C_{C}}{\partial z}$$

(19)

where $C_{C}$ is the concentration of C in moles per volume, $D_{C}$ is the diffusional flux of C. Then, the moving velocity of the PE–$\alpha$/PE–$\theta$ interface is given by
Fig. 14. Simplified diffusion geometries to simulate the growth of paraequisilibrium cementite (PE-\(\theta\)) at the lath martensite (\(\alpha\)) boundaries. From the mass balance consideration within the cell ABCD, the growth of one PE-\(\theta\) particle in a lath of 1\(\mu\)m wide (shown in a) is equivalent to the growth of one PE-\(\theta\) particle at the interface two laths of 0.5\(\mu\)m wide each (shown in b).

\[
\nu_s = \frac{J_{c,PE-\alpha}}{C_{c,PE-\alpha}^{0.25}}
\]

(21)

A fundamental assumption is that the thermodynamic and kinetic parameters of the lath martensite phase are the same as that of the ferrite phase. A further simplification is that even though the interlath PE-\(\theta\) particles nucleate and grow at the lath boundaries, 1-D growth simulations are carried out based on the lattice mobility in PE-\(\alpha\). Under paraequilibrium condition, the cementite phase is stoichiometric with respect to Z and C; therefore, diffusion within PE-\(\theta\) need not be considered.

Fig. 15(a) shows the simulated growth of a PE-\(\theta\) particle and C profile in the matrix of C3B at 755 K as a function of time. The initial C content and the final (after complete growth of the PE-\(\theta\) particle) are marked as \(X_0,_{C}^{\alpha}\) and \(X_{C}^{PE-\alpha}\), respectively. Based on the diffusion geometry shown in Fig. 14(a), the PE-\(\theta\) particle grows to about 22 nm. This is in very good agreement with the observed thickness of 20 nm for the same alloy, as shown in Fig. 6. We believe that a major reason for such a good agreement is due to the fact that the PE-\(\theta\) particles in C3B are primarily interlath type. Fig. 15(b) shows the growth kinetics of PE-\(\theta\) for a time period of 10 s. It is seen that the initial parabolic kinetics continues up to about 55% of the transformation. This is despite the fact that the far-field supersaturation drops below the initial supersaturation even before the 55% transformation. As shown in Fig. 15(b), most of the growth of PE-\(\theta\) particles takes place within about 7 s, and the extent of growth after that is negligible. On the other hand, based on a similar simulation for 1605-2C it is found that most of the growth of PE-\(\theta\) particles takes place within about 3 s where the PE-\(\theta\) particle grew up to about 35 nm. These results will be discussed further in terms of the effect of substitutional alloying elements on the diffusivity of C. Nonetheless, the simulations demonstrate that once the PE-\(\theta\) particles nucleate, their growth rate determined by C diffusion alone is rather fast.

In Fig. 15(b), the initial parabolic growth kinetics is characterized by a time-independent rate constant, and the deviation from this behavior during the later stages of growth can be described by a time-dependent rate constant, due to a rapid decrease in driving force during the growth. In Fig. 15(a), it may also be noted that after complete growth of the PE-\(\theta\) particle, the C content in the matrix has decreased about two orders of magnitude. This causes about a 40% reduction in the driving force for the nucleation of the coherent\(\alpha\)/C phase that gives rise to secondary hardening [25]. The moving velocity of the PE-\(\alpha\)/PE-\(\theta\) interface is shown in Fig. 15(c). Initially the interface velocity is very high because of a very high driving force. As the supersaturation of the matrix decreases during the growth of PE-\(\theta\) particle, the interface velocity also gradually decreases, and finally, at the later stages of growth, the interface velocity drops precipitously.

The results of analogous calculations for the Fe-0.41C-3Mn-2Si alloy are shown in Fig. 16(a)-(c). Due to much higher C content in this alloy the PE-\(\theta\) particle grows up to 52 nm. Babu et al. [18,19] observed PE-\(\theta\) platelets that were about 20 nm thick. A much higher predicted thickness than the experimental value is due to the fact that
Fig. 15. The simulated paraequilibrium growth of PE-θ having a flat interface in C3B at 755 K; (a) an enlarged part of the cell showing the carbon profile in the matrix (PE-α). The Y-axis is in logarithmic scale to clearly show the carbon profile within PE-α. The initial carbon content and that after the completion of paraequilibrium growth (or transformation) are marked as $X_C^{PE}$ and $X_C^{PE_{\theta}}$, respectively; (b) the thickening kinetics of the PE-θ particle for up to 16 s. The dotted line shows the thickness of PE-θ if the initial parabolic kinetics would have continued for the entire time period. (c) the PE-θ/PE-α interface velocity as a function of the thickness of PE-θ.
Fig. 16. The simulated paraequilibrium growth of PE-\(\theta\) having a flat interface in FeMnSiC at 623 K: (a) an enlarged part of the cell showing the carbon profile in the matrix (PE-\(\alpha\)). The Y-axis is in logarithmic scale to clearly show the carbon profile within PE-\(\alpha\). The initial carbon content and that after the completion of paraequilibrium growth (or transformation) are marked as \(X^\text{eq}\) and \(X^\text{eq+}\), respectively. (b) the thickening kinetics of the PE-\(\theta\) particle for up to 20 s. The dotted line shows the thickness of PE-\(\theta\) if the initial parabolic kinetics would have continued for the entire time period. (c) the PE-\(\theta\)/PE-\(\alpha\) interface velocity as a function of the thickness of PE-\(\theta\).
our simulation considers only the interlath growth, while both intra- and interlath particles were observed experimentally.

Deviation from the initial parabolic growth behavior, shown in Figs. 15b and 16b, could also arise from hard and soft impingement effects. However, these effects are absent in our simulation as we have considered the growth of only one particle. In other words, our growth simulations demonstrate that the deviation from the initial parabolic growth law is solely due to the decrease in available driving force. In reality, this situation may arise in systems containing a low volume fraction of the growing phase where the impingement effects are minimal, if not absent.

Comparing the simulated interface velocities in C3B and FeMnSiC alloys, we find that at a comparable thickness of PE-θ the interface velocity in FeMnSiC alloy is higher compared to C3B. For example, at a thickness of 10 nm the interface velocities are 3.9×10^{-8} m/s in FeMnSiC and 1.0×10^{-8} m/s in C3B. Similarly, at 50% transformation the interface velocities are 1.4×10^{-8} m/s in FeMnSiC and 9.7×10^{-9} m/s in C3B. This is despite the fact that the FeMnSiC alloy is tempered at a temperature of 132 K lower than C3B, and the chemical driving force is less in FeMnSiC compared to C3B.

We attribute this behavior to the influence of alloy chemistry on the C flux and its diffusivity. The FeMnSiC alloy has much higher C content, 0.41 mass% compared to 0.16 mass% in C3B. This partly accounts for higher flux (or the interface velocity). The second important factor is the role of alloying elements on the diffusivity of C. The tracer diffusivities of C in pure α-Fe at 623 and 755 K are 1.76×10^{-13} m²/s and 3.02×10^{-12} m²/s, respectively. In other words, based on the tracer diffusivity of C one would expect that the interface velocity in C3B tempered at 755 K would be much higher compared to the FeMnSiC alloy tempered at 623 K. Since C3B is a highly alloyed steel, it is appropriate to compare the diffusivity of C in the alloys. The chemical diffusivities of C in fully supersaturated α solid solution are 1.6×10^{-13} m²/s in FeMnSiC alloy at 623 K and 3.0×10^{-13} m²/s in C3B at 755 K. The latter value is about one order of magnitude less than the tracer diffusivity of C in pure α-Fe. We find that Co has a strong effect in reducing the diffusivity of C in ferrite. For this reason, it takes less time for the PE-θ particle to grow 35 nm in 1605-2C containing 16 mass% Co compared to 22 nm in C3B containing 28 mass% Co.

Even though our model calculations do not consider any resistive or dissipative forces, such as the interfacial energy, strain energy and a finite interface mobility, we conclude that these simulations shed some light on the complex interplay between alloy composition and tempering temperature on the growth kinetics of PE-θ.

5. Conclusions

Precipitation of paraequilibrium cementite during early stages of tempering of two model UHS steels at 755 and 783 K is confirmed by analytical electron microscopy. Furthermore, the temporal evolution of the composition of precipitated cementite is investigated up to 1 h of tempering at 755 K, and the data suggest a gradual transition from the paraequilibrium state towards the orthoequilibrium state.

A thermodynamic parameter, consistent with the two-sublattice model for cementite, is proposed to describe the effect of Si on the phase stability of cementite. The model parameter is estimated utilizing the known phase equilibria of the Fe-Si-C and Co-Si-C systems. The model parameter is consistent with the fact that under orthoequilibrium conditions Si does not partition to cementite, yet there is sufficient driving force for the nucleation of paraequilibrium cementite in the presence of Si in certain alloys.

The results of simulation of the growth of a cementite particle under paraequilibrium with the fault martensitic matrix is presented for C3B and FeMnSiC alloys. It is shown that once nucleated the full growth of paraequilibrium cementite, determined by C diffusion alone, takes place in the time scale of seconds. The model simulations do not consider any resistive or dissipative forces, such as the interfacial energy, strain energy, or a finite interface mobility, and as a result, the interface velocities represent an upper limit under the available chemical driving force. Nonetheless, the
simulations help elucidate the complex interplay between alloy composition and tempering temperature on the growth kinetics of PE-$\theta$.

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References