Revisiting the Structure of Martensite in Iron-Carbon Steels

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A model is developed to describe the formation and crystal structure of martensite in quenched Fe-C steels based on the extensive published literature on the subject. Unique changes in the properties and structure of martensite are shown to occur at 0.6 mass% C, designated as the H-point. The concept of primary and secondary martensite is introduced in order to indicate that two different, sequential, martensites will form during quenching of Fe-C steels above 0.6 mass% C. Below 0.6 mass% C, only primary martensite is created through the two sequential steps FCC → HCP followed by HCP → BCC. Primary martensite has a lath structure and is described as BCC iron containing a C-rich phase that precipitates during quenching. The HCP transition phase is critical in interpreting the two martensite structures based on the premise that the maximum solubility of C in the HCP phase is 0.6 mass%. Primary martensite continues to form at compositions greater than 0.6 mass% C with the creation of a carbon-rich BCT phase. This is followed by the start of secondary martensite which forms at the M_s (martensite start temperature) and creates the traditional BCT plates adjoining retained austenite. Both martensites are predicted to co-exist at the highest C contents. A quantitative model, based on the specific volume of the various phases obtained after quenching, has been used to calculate the composition of the precipitated C-rich phase for a 0.88 mass% C steel. It is predicted that the carbon-rich phase is either diamond or η (Fe_2C) carbide. [doi:10.2320/matertrans.MRA2007338]

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1. Introduction

The quenching of Fe-C steels to produce material characterized by exceptionally high hardness has been known for thousands of years.^{1,2)} Yet to this day the quenching process remains a mystery with respect to the specific changes that take place. The published literature on this subject has been voluminous and has been summarized by Morris Cohen in two review papers,^{3,4)} and more recently by Wayman⁵⁾ and by Krauss.⁶⁾ The dominant structure developed after quenching into ice water or brine from the austenite range is martensite, a very complex constituent. Its structure has been described as massive, cubic, lath-like, lenticular, subgrain-containing bundles at low C contents (i.e. up to 0.6 mass% C).⁵⁻⁹⁾ At higher C contents (greater than 1 mass% C) the martensite structure changes to an acicular, plate-like structure adjoining regions of untransformed austenite.^{9,10)} Between about 0.6 and 1.0 mass% C, a mixture of both lath-like and plate-like structures is observed⁹⁾ implying that two uniquely different structures occur simultaneously, or sequentially, during the quenching process. Other unexplained changes relate to the crystal structure of martensite and austenite as influenced by C content. For example, it has been shown that martensite has a BCC structure in the low carbon range up to 0.6 mass% C.¹¹⁻¹³⁾ Martensite, however, changes suddenly to a BCT structure above 0.6 mass% C with a c/a ratio increasing linearly with increase in the C content. This sudden change in crystalline form of martensite at 0.6 mass% C has been a puzzle that will be revisited in this paper. These dilemmas are further compounded by considering the M_s temperature; the temperature that has been used to describe the start of the transformation to martensite. The M_s temperature is in the order of 200°C for Fe-C steels in the range 0.8 to 1.0 mass% C.⁹⁾ This is a very low temperature. What structural changes, if any, occur during the approximate

500°C drop in temperature from the start of the equilibrium transformation temperature (723–750°C) to the M_s temperature? The recent work of Yonemura *et al.*^{14,15)} provides clues to answer this question. In this work, *in situ* observations of the structural changes during quenching of an Fe-0.88 mass% C steel were made with time-resolved X-ray diffraction. It will be shown that these observations provide insight to some of the questions on the structure of martensite.

2. Results of Quenching Studies on 0.88 mass% C Steel

Yonemura *et al.*^{14,15)} have studied changes in the structure of Fe-C steels as they solidify from the molten state during welding. Their work involves *in situ* measurements taken using a time-resolved, X-ray diffraction technique as pioneered by Babu *et al.*^{16,17)} and Elmer *et al.*¹⁸⁾ The uniqueness and value of the Yonemura *et al.* study is the use of a very fast detector with very fine time resolution for capturing individual diffraction peaks during quenching. The exposure time was quoted as 0.15 second, and thus the resolution of structural changes was achieved during rapid quenching. The weld metals in their case were two Fe-C steels (0.02 and 0.88 mass% C). The welding process is a classic example where high cooling rates take place. The rapid cooling is a result of the heat absorption by the cold steel adjoining the molten weld leading to rates as high as several hundred °C s⁻¹.¹⁴⁾ The experimental observations of Yonemura *et al.* provided *in situ* diffraction patterns of the phase transformation process during rapid weld cooling. The experimental procedure was possible because of the availability of intense X-ray beams from synchrotron storage rings. The change in structure was monitored by following the change in the lattice parameter of austenite during the rapid quench. It would appear that this is the first time such data have been reported for Fe-C steels.

Fig. 1 The lattice parameter of austenite as a function of temperature during rapid cooling in 0.88 mass% C steel as determined by Yonemura *et al.* The M_s temperature of 220°C for this steel is shown in the figure, together with the lattice parameter of austenite documented by Cheng *et al.* from quenching studies on the same material to ice-brine.

The data of Yonemura *et al.* is shown in Fig. 1 and is plotted as the lattice parameter of austenite as a function of temperature during rapid cooling of the molten Fe-0.88%C steel. The specific data points are given as open symbols covering the range from 1500°C and ending with their lowest temperature of measurement at 300°C. The authors stated that 300°C was the completion of transformation for their 0.88 mass% C material. The cooling rate change during the experiment is given at the top of the figure, and is estimated to be 100°C s⁻¹ in the transforming region. The authors concluded that the austenite was transforming to ferrite that contains particles (such as cementite); these are the expected products observed in the equilibrium Fe-C phase diagram. The authors related the slope of the line from the beginning of transformation to 300°C, i.e. the shrinkage rate, to the known expansion curve for a ferritic steel of low C content. In addition, the authors analyzed their X-ray data and concluded that the austenite crystallites that formed from the melt were approximately 5 to 10 nm in size, and the particles were approximately 1 to 2 nm in size. The authors did not mention martensite in the analyses of their work but they did note the presence of ferrite diffraction lines beginning at about 725°C.¹⁵⁾

3. Discussion of Results of Yonemura *et al.*

The present authors have added a vertical line locating the M_s temperature at 220°C⁹⁾ for the 0.88 mass% C steel in Fig. 1. This M_s temperature is 80°C below the lowest measured temperature by Yonemura *et al.* In addition, a datum point, indicated by the filled circle symbol, is added to their graph at 0°C. The austenite lattice parameter for this point was calculated from the known lattice parameter in retained austenite for 0.88 mass% C steel when quenched in water or ice-brine.¹⁹⁾ It is significant to note that the data of Yonemura *et al.* extrapolate closely to this added datum point. This observation indicates continuity between the

findings of Yonemura *et al.* and the known transformation that takes place at the M_s temperature. The structure of quenched high C steels is known to contain retained austenite; as an example, a brine-quenched steel of approximately 0.88 mass% C content contains about 12% retained austenite.⁹⁾ Since there is 100% austenite at about 725°C, it is possible to estimate the retained austenite at any temperature of cooling, assuming a linear dependence of retained austenite with temperature. As noted in Fig. 1 the predicted amount of retained austenite at the last measured point of Yonemura *et al.* is 47%. The predicted amount of retained austenite is 38% at the M_s temperature. Total transformation of austenite is predicted at -97°C. This prediction is not far from the low value of 4% retained austenite after refrigeration in liquid nitrogen (-196°C).²⁰⁾

It is generally considered that the M_s temperature represents the true start of transformation of austenite. The basis for this is the observation of a sudden change in microstructure and properties during rapid quenching only at the M_s point. An example is the thermometric work of Greninger for 0.84 mass% C steel²¹⁾ where the result revealed only one inflection in the quenching process. The result was shown to occur at the same temperature, 220°C irrespective of the cooling rate, in one case at 3600°C s⁻¹ and the other at 100°C s⁻¹. The inflection (i.e. thermal arrest) was attributed to heat evolution from martensite formation. The distinct change in slope of the lattice parameter versus temperature curve of Yonemura *et al.*, however, supports the idea that a pre- M_s transformation occurs. It will be shown that a primary martensite product is obtained in the pre- M_s range followed by secondary martensite product at and below the M_s . A thermal arrest may not be expected because the transformation occurs gradually over a wide range of temperature. The rate of austenite depletion is about one percent for every 8°C drop in temperature.

4. Proposed Mechanism of Transformation in Carbon Steels

The new findings of Yonemura *et al.* provide a missing link to understanding what is happening during water quenching of high carbon Fe-C steels from the austenite range. The results indicate that two sequential stages occur during quenching. The first stage is represented by the Yonemura *et al.* data from 725°C to near the M_s temperature; the authors associate this with precipitation of a carbon-rich phase in a BCC ferrite matrix. This first transformation is a martensite product and it is proposed to designate this product as M_p with the subscript p representing particles. The prediction of a carbon-rich phase is related to auto-tempering that is frequently discussed in quenched martensite.^{3,4)} "Auto-tempering" refers to the formation of particles during the quenching process—not during the subsequent process of tempering after quenching. The second transformation is represented by the formation of martensite where, in this case, the body-centered-tetragonal structure of ferrite is observed. This transformation will be designated as M_{BCT} with the subscript BCT representing the body-centered-tetragonal structure of iron. The M_{BCT} temperature is the same as the M_s temperature. There is additional support for

Fig. 2 The c/a ratio for martensite in quenched Fe-C and Fe-N steels as a function of at% C or N. The weight percent of C is given in the upper portion. The term wt%C is used interchangeably with mass%C in this paper.

the notion of the two proposed transformations. The work of Esser *et al.*, published in 1933,²²⁾ describes the changes in magnetic properties during rapid quenching of Fe-C steels. The authors showed, for a 0.906 mass% C steel quenched at $200^{\circ}\text{C s}^{-1}$, a ferromagnetic transformation from 590 to 400°C , followed by a discontinuity in the ferromagnetic response and then another ferromagnetic transformation from 260 to 110°C .

These observations are the basis for a quantitative model that explains the contribution of each of the martensitic products to the changes in properties. It will be shown that the different martensitic structures obtained during rapid cooling are related to basic and abrupt changes in the structure and properties of quenched Fe-C steels as a function of C content. Specifically, the present authors¹¹⁾ have investigated the changes in the lattice parameter of martensite in quenched Fe-C steels as a function of C content. It was shown that an abrupt change takes place in the lattice parameter of martensite at a specific C content (0.6 mass% C); an observation that has generally been ignored. Figure 2 shows data from a number of investigators^{12,13,23–28)} on the c/a ratio of quenched steels based not only on Fe-C alloys but also on Fe-N alloys. It is seen that the c/a ratio is unity from zero to the same atom percent value of either interstitial C or N, at a value 2.75 atom percent. The c/a ratio then abruptly changes from unity to a value of ~ 1.03 . Subsequent increases in solute C contents lead to ever increasing values of c/a that are related to the BCT structure of martensite. The value of 2.75 at% C translates to 0.6 mass% C in Fe-C steels. This specific discontinuity in the lattice parameter clearly demarks the boundary between two different transformation processes. Surprisingly, discussion in the literature of this anomaly is scant. The discontinuity is invariably omitted in figures either when the parameters are plotted as a ratio of c/a shown in Fig. 2, or if c and a are plotted independently.

4.1 Explanation of the 0.6 mass% C discontinuity

A model explaining the anomaly at the 0.6 mass% C (2.75 at% C) point was proposed by Zener²⁹⁾ and has been discussed by other researchers.^{5,12,13,30,31)} Zener summarized

Fig. 3 The c and a parameters for martensite in quenched Fe-N steel. The lattice parameters are seen to be the same (0.2868 nm) from 0.22 to 2.5 at% nitrogen.

his model by concluding that “the transition of martensite from a tetragonal lattice to a cubic lattice is interpreted as a change from an ordered distribution of carbon to a random distribution”. The proposal requires interstitial C to be in random solution from nearly zero to the break point (0.6 mass% C) with the lattice parameter increasing with increase in the amount of C in solution. This prediction, however, is not observed as is shown in Fig. 3 that is taken from the work of Owen and Bell^{12,13)} for the Fe-N steels. Rather, the lattice parameter is shown to be a constant with increasing N interstitial content, remaining at $a = 0.2868$ nm for 0.50, 1.50 and 2.50 at% N. The lattice parameter of pure Fe is lower than this value at 0.2864 nm.³²⁾ The difference between the two values is a consequence of lattice expansion from the N in solution with the maximum solubility in Fe of 0.4 at%.³³⁾

Results of this type have led the present authors to propose that C-rich phase is in fact created during quenching. This takes virtually all of the interstitial atoms out of solution—hence only the BCC structure is observed. The same conclusion is reached with the data of Fig. 2 in which the work of Campbell and Fink²³⁾ on quenched Fe-C steels reveals the presence of the BCC structure at low C contents. X-ray analyses by Honda and Nishiyama²⁴⁾ have also confirmed the presence of the BCC structure at low C contents. The remarkable similarity of the Fe-C and Fe-N results when compared on an at% basis suggests an electronic contribution to the observed pattern. The similarity is supported by Jack who prepared a series of carbo-nitrides of Fe in which C and N atoms are freely interchangeable. These particles have compositions ranging from Fe_2X to Fe_3X where X is C or N.^{34–37)}

The possible influence of C and N on the structure, however, does not explain the abrupt break shown in Figs. 2 and 3. It is the crystal structures that are known to exist in Fe, and the influence of the electronic states of these structures, that provide an explanation of the observed transformations. The present authors have utilized the Engel-Brewer theory of crystal structures of the elements.¹¹⁾ The details of this electronic theory are described by Brewer³⁸⁾ and by Hume-

Rothery.³⁹⁾ The theory states that the s and p electrons control the crystal structure, with a valence of one for BCC elements, of two for HCP elements, and of three for FCC elements. It is proposed¹¹⁾ that the transformation of γ -Fe (FCC) to α -Fe (BCC) will be more efficient through the sequence of FCC to HCP to BCC. In fact, this view is supported from the pressure-temperature diagram for pure Fe, in which all three phases are shown to co-exist (the triple point is at $P = 11.5$ GPa and $T = 487^\circ\text{C}$).^{11,40)} Thus, above this critical pressure, the transformation will be FCC ($V = 3$) to HCP ($V = 2$) to BCC ($V = 1$) upon cooling from the γ range. The HCP structure has been designated as the ε phase and is paramagnetic; the same is true for the FCC structure. It is proposed that the internal pressure generated from the volume change associated with the change in crystal structure (a minimum of 11.5 GPa for pure Fe) is a critical variable in causing formation of the HCP structure. The FCC $\rightarrow$ HCP and HCP $\rightarrow$ BCC transformation take place by an athermal, thermodynamically driven, shear controlled process. The break point in the lattice parameter at 0.6 mass% C has its origin in considering the maximum solubility limits of carbon in the various phases of iron. These limits are 2.1 mass% C for FCC ($V = 3$), and 0.02 mass% C for BCC ($V = 1$). The solubility limit of 2.1 percent C is known as the E point. The expected solubility limit for carbon in the HCP phase ($V = 2$) is between the two limits. The maximum solubility limits are related to the volume available in the interstices of the respective crystal structures, FCC, HCP, and BCC. It is proposed that 0.6 mass% C is the maximum solubility limit in the HCP structure of Fe-C steels. In the case of Fe-N steels, the solubility limit in mass% is 0.75%. This solubility limit, when expressed in at% is 2.75%, and is designated as the H point in Fig. 3.

The value of the H point can be influenced by changes in alloy content or by processing conditions. Winchell and Cohen⁴¹⁾ have shown that large Ni additions will decrease the H point to about 0.2 mass% C. This change may be a result of Ni and its influence on decreasing the stability of the HCP phase when containing C. In another example, the HCP phase appears to be unstable when splat quenching is used to transform Fe-C steels from the liquid state. Cadeville *et al.*⁴²⁾ showed the formation of the body-centered tetragonal structure down to very low carbon concentrations with the H point at about 0.2 mass% C. In this case, the unexpected structure may be caused by the additional transformation of liquid to solid or by the rapid quenching from the splat quenching process. Seetharaman and Krishnan⁴³⁾ have shown that plastic deformation of an austenitic 316 stainless steel will transform the FCC structure to a paramagnetic HCP structure. Then, with further straining, the HCP structure will transform to a ferromagnetic BCC structure. Similar changes were observed by Lee, Fukuda and Kateshita⁴⁴⁾ for solution treated and quenched SUS304L austenitic stainless steel. In this case, all three phases were shown to coexist by long time tempering at 77 K (without deformation).

4.2 Structure of primary martensite in quenched Fe-C steels

Primary martensite is the structure of quenched Fe-C steels in the low carbon range from nearly zero to the

H-point. It is usually described as lath martensite. This structure is complicated in detail⁷⁾ and is identified as elongated grains/cells 0.5 to 1 μm in width in TEM examination. Another structure, twin martensite, is often observed as a dispersed structure within the lath martensite. The present model proposes that two transformations take place during the quenching process that contributes to the final structure. The first transformation converts the face-centered-cubic solid solution to the hexagonal-close-packed solid solution. There is a volume decrease during transformation, in the order of $\Delta V_{\gamma-\varepsilon} = -0.13$ cc/mole measured in pure iron.⁴⁵⁾ The transformation requires a shearing process that converts the “*abcbcb*” stacking of atoms in FCC to “*ababab*” stacking in HCP and is accompanied by a relocation of carbon atoms in the process. Latent heat of transformation occurs in the process. The second transformation is the HCP phase transforming to the BCC phase where lath martensite is created. A large volume increase occurs in this transformation since it is known that $\Delta V_{\varepsilon-\alpha} = +0.34$ cc/mole in pure iron.⁴⁵⁾ Rejection of carbon from the BCC phase (auto-tempering) to form a carbon-rich phase will become part of the martensite structure. A large latent heat of transformation will take place. The details of such transformation apparently have not been pursued. The presence of twin martensite is often discussed but its relation to the lath martensite remains unresolved. Quantitative studies on the fraction of twin and lath martensites have been documented by Speich, Warlimont and Leslie⁴⁶⁻⁴⁹⁾ and by Kelly and Nutting.⁵⁰⁾ The volume fraction of twin martensite is nearly zero at low carbon contents, and increases to 3% at 0.2 mass% C, to 12% at 0.4 mass% C, and to 25% at 0.6 mass% C.

Esser *et al.*^{22,51)} have demonstrated the presence of two transformations in Fe-C steels at cooling rates of 200–15,000°C per second. Typical cooling rates obtained in ice-brine quenching are about 300°C per second. The authors evaluated many carbon compositions including 0.17, 0.24, 0.32 and 0.47% C. In these experiments, the quenching rates were about 1000°C per second. The first transformations were observed at 560, 590, 600 and 480°C respectively. These temperatures are all above the traditionally recorded M_s and are related to the proposed FCC to HCP transformation. The second transformations were observed at 420, 390, 370 and 320°C respectively. These temperatures are below the traditionally recorded M_s , although the values converge towards the M_s with increase in carbon content. Nevertheless, it is proposed that the second transformation is lath and twin martensite and is created during the HCP to BCC transformation.

Mirzayev *et al.*⁵²⁾ described transformations in iron-carbon steels below the H-point when quenched at extremely rapid cooling rates, i.e. 30,000 to 300,000°C per second. At these high quenching rates they show two transformation events, both occurring below the conventional M_s . For example, whereas the first transformation for the 0.34 mass% C steel was 600°C for the Esser study, it was at 410°C for the 0.32 mass% C steel of Mirzayev *et al.* The second transformation occurred at 350°C. These results suggest that at high quench rates the proposed FCC-HCP transformation is by-passed. The authors state that the first transformation

creates a lath structure and the second creates a plate structure. Plate martensite is usually related to body-centered tetragonal martensite that is not normally observed until above the H-point. Apparently the very high cooling rates used, in excess of $30,000^{\circ}\text{C}$ per second, enabled the formation of BCT martensite in the low carbon range. These results explain the splat-quenching work of Cadeville *et al.* who showed X-ray evidence for a BCT structure at carbon contents below 0.6 mass% C. Mirzayev *et al.* did not describe X-ray diffraction crystal structures of their quenched materials but did show the microstructures of their samples at two quench rates, 10^4 and $3 \times 10^5^{\circ}\text{C s}^{-1}$. A lath-like structure was shown with no obvious evidence for a plate structure, with a more dispersed appearance at the highest cooling rate. A significant observation is that the high hardness of the quenched steels was increased by increasing the quenching rate indicating that finer structures were created. Ultra-high quenching rates, in excess of $10^5^{\circ}\text{C s}^{-1}$, may find useful applications.

Wilson⁵³⁾ and Zhao⁵⁴⁾ have described the plate martensite structure of Mirzayev *et al.*, as twin martensite. This terminology may not be appropriate. This is because twin structures are seen to be only a part of the whole structure. Wilson concluded that twinned martensite was the only structure observed at and above 1% carbon. TEM studies by Kelly and Nutting show about 50% twin structures and 50% non-twin structures for both 1 and 1.4 mass% C steels. Neither Wilson nor Zhao reference the work on the quantitative study of twinned martensite^{46–50)} in quenched low carbon steels.

4.3 Interaction of primary and secondary martensite on structure

The conclusion of the above analyses is that there will be a mixture of three distinct kinds of martensite forming beyond the H-point. The first two transformations during quenching are related to primary martensite. Upon completion of primary martensite formation, the next transformation begins related to the M_{BCT} process. This transformation produces secondary martensite. Each transformation contributes to a specific structure.

The fine structures in primary martensite, consisting of fine cell structures, twins, and a C-rich phase as plates, are responsible for the very high strengths of martensitic steels in the low to intermediate C range.^{8,47,52)} The C-rich phases that are first observed in primary martensite, identified by X-ray analysis⁵⁵⁾ are described as ultra thin, two dimensional plates rather than spherical particles. Kelly and Nutting⁵⁰⁾ noted carbides in quenched 0.1 mass% C steel that formed by auto-tempering. The terms “plate” and “particle” are used interchangeably to denote the formation of a C-rich phase. The specific mechanism of transformation in primary martensite is likely related to the shear mechanisms such as those described by Kurdjumov and Sachs.⁵⁶⁾ Primary martensite will also be observed above 0.6 mass% C but with diminishing volume fraction and diminishing influence on properties with increase in C content. The structural changes that take place in primary martensite in the high C range require additional transformations and these are described in detail in section 4.4.

Secondary martensite will begin to form at 0.6 mass% C, and increases in amount with increase in C content. It involves only one transformation, but it is always preceded by the formation of primary martensite. The structure of secondary martensite results from the formation of the BCT form of Fe, a solid solution of C in α -Fe. This transformation is described by the Bain transformation process⁵⁷⁾ and is related to a compression-stress-directed transformation. Shear mechanisms are considered to be un-important in the formation of BCT Fe. The C content of the steel determines the c/a ratio; the higher the C content, the greater the value of the c/a ratio. The structure of BCT martensite is an acicular, plate-like structure. Ultrafine twins are observed in some of the plates. It does not have the fine elongated cell structure of lath martensite. It is commonly described as plates impinging on each other with retained austenite adjoining the plates.⁹⁾

4.4 Models illustrating proposed structure changes during quenching

Two dimensional models illustrating the expected structures during primary and secondary martensite formation in the 0.88 mass% C steel are shown in Figs. 4 and 5. The crystallite size of 10 nm for the austenite phase was selected as proposed by Yonemura and colleagues. The boundary is considered to consist of a loose knit array of dislocations and is the source of the nucleation site for transformation. Figure 4 depicts the sequential transformations in forming lath structure of primary martensite leading to the creation of three phases, i.e. enriched BCT or enriched FCC, BCC and C-rich phase. The expected distribution of crystal structures are shown in Fig. 5 for (1) the completion of primary martensite formation that includes twin and lath martensites, and (2) the completion of secondary martensite formation at room temperature containing retained austenite. These structures are the basis of a quantitative model described in Section 4.5 that leads to a prediction of the unknown C-rich phase.

Figure 4 illustrates the proposed crystal structure changes in the formation of primary (lath) martensite from FCC austenite in the 0.88 mass% C steel. This is the structure that will form for all hyper H-point carbon steels. The two different scenarios, labeled as A and B in Fig. 4, show the same transformation process with only minor changes related to one transformation step. The transformation is proposed to occur by a lamellar transformation. The model labeled as A—step 1 in Fig. 4 illustrates the first of two transformation steps. The first transformation shows the formation of the HCP phase containing 0.6 mass% C (green color) and a carbon-enriched phase of FCC austenite (yellow color). The transformation $\text{FCC} \rightarrow \text{HCP}$ is readily achieved involving shear displacement in the close-packed plane in the FCC austenite phase that becomes the close-packed plane in the HCP phase. The enriched FCC phase is created because of the rejection of carbon in the newly created HCP phase that can only contain 0.6 mass% C into the 0.88 mass% C austenite. The carbon content of the enriched austenite is calculated from the conservation of mass. The total weight of 0.88 mass% C is equal to $(0.6/0.88) [\text{HCP}]_{0.6 \text{ mass\% C}} + (0.28/0.88) [\text{FCC}]_{x \text{ mass\% C}}$ where x is the mass% C in the enriched austenite phase. The result is an enriched

Fig. 4 Transformations in primary martensite for the case of the 0.88 mass% C steel. The example in A, step 1, shows the FCC phase transforming to HCP phase of 0.6 mass% C (green) with enriched FCC phase (yellow). This is followed by step 2, with HCP phase transforming to BCC phase (blue) plus carbon rich phase (black), and with enriched FCC phase transforming to enriched BCT phase (red). Example B shows the modified model on the basis that the enriched austenite remains stable.

1.475 mass% C austenite. The enrichment means that the carbon atoms are more closely spaced than in the initial inter-carbon atom distance. Since there is no time for diffusion, the rearrangement is achieved by mechanical transport of carbon atoms by lattice shearing actions and by changes in the interlayer spacing. The lamellar transformation structure is favored over a particulate one because only a single nucleation step is required and the propagation completes the first transformation step. On the other hand, a particulate structure, namely a distribution of spherical particles of the enriched FCC phase in a matrix of the HCP phase would require many nucleation steps.

Upon completion of the formation of the HCP phase with the carbon-enriched FCC phase, the second transformation begins. This is shown in A—step 2 of Fig. 4 that illustrates formation of the second transformation. One change is the formation of the BCC phase (blue) containing plates of the C-rich phase (black) from the disappearing HCP phase (green). As with the formation of the HCP phase from the austenite, the phase change HCP → BCC involves shearing of the lattice during transformation allowing C-rich phase to form in the BCC matrix. The other simultaneous change is transformation of the enriched FCC phase (yellow) to an identically enriched BCT phase (red). This structure change occurs by the Bain transformation involving compression deformation rather than shearing thus preserving the BCT structure rather than a carbon-rich phase formation in a BCC phase. A large volume increase is expected during the second transformation because of the creation of the BCC/BCT phase. The second transformation creates a mixture of lath and twin martensite.

The proposed model will find support in quantitative analyses of the quenched martensite structure to be described later in the present paper. It is worth considering, however, that the enriched FCC phase may be more stable than the enriched BCT phase (Fig. 4A—step 2). Figure 4B—step 2 shows the modified model on the basis that the enriched austenite remains stable. Since austenite has a much smaller specific volume than the BCT phase, the proposed quantitative analysis of the quenched martensite structure will differ for the two different models.

The proposed structures in primary martensite should persist at carbon contents above 0.6 mass% C, but with a decreasing weight fraction of lath structure with increase in carbon content. Thus, the weight ratio of 0.60/0.88 = 0.68 for the 0.88 mass% C steel will decrease to 0.28 for a quenched 2.1 mass% C steel. This interpretation has not been proposed in previous studies. It is generally stated that the lath martensite structure is no longer part of the transformation structure above about 1 mass% C.^{6,9)} Kaputkin *et al.*,⁵⁸⁾ however, quenched a 1.85 mass% C steel,

Fig. 5 The proposed distribution of phases during quenching of Fe-0.88 mass% C is illustrated. (a) Completion of formation of primary martensite, with the remainder shown as untransformed austenite. A distribution of about 75% lath martensite and 25% twinned martensite (symbol T) is shown. (b) The proposed structure at room temperature is shown with completion of formation of secondary martensite. The BCT phase (pink) contains 0.88 mass% C, and the remainder is retained austenite.

and determined the presence of 82% austenite with 18% martensite. The martensite was described as lenticular, and that is usually associated with lath martensite (primary martensite).

Figure 5 illustrates schematically the distribution of structures during quenching of the 0.88 mass% C steel. Figure 5(a) illustrates the completion of the formation of primary martensite that is considered to occur at 300°C, see Fig. 1. The two principal microstructures that form are twinned and lath martensites. The proportion is given at 25% for twinned martensite and 75% for lath martensite based on the values given by Speich and Leslie.⁴⁸⁾ These structures represent 63% of total transformation microstructure at room temperature. The specific volume of the twinned martensite is expected to be about the same as that for lath martensite. The microstructure consists of four phases: the BCC phase, the C-rich phase, the enriched BCT phase, and the untransformed FCC austenite. Figure 5(b) shows the distribution of primary and secondary martensite with retained austenite after quenching to room temperature. The distribution of the three regions is 63% for primary martensite, 25% for secondary martensite and 12% for retained austenite. This figure illustrates why X-ray analyses readily detect the presence of retained austenite and of the 0.88 mass% C BCT martensite since they are grouped in relatively large region of the quenched structure. On the other hand, primary martensite contains three phases, each of them in the nano-size range and their mutual interaction, would make for great difficulty in detection. It is possible, that powerful X-ray or electron diffraction techniques could provide evidence for the proposed structures. The predicted phases could be deduced by their contribution to density changes.

Practitioners in heat-treating have utilized the two transformation steps described in Figs. 4 and 5. A process called austempering⁵⁹⁾ involves quenching an Fe-C steel in an appropriate medium at a temperature just above the M_s temperature, then held in the medium until the temperature is uniform throughout, followed by cooling in air. Subsequent treatment, such as cryogenic treatment or mechanical working follows.

4.5 Relation of the H point to structure and properties of quenched Fe-C steels

Retained austenite is an important portion of the structure of martensite. The early history of retained austenite in quenched Fe-C steels is described by Magner *et al.*⁶⁰⁾ Figure 6 summarizes the influence of carbon on the amount of retained austenite after martensite formation in Fe-C steels.^{9,20,61–66)} The results indicate that little or no retained austenite is observed for quenched Fe-C steels below the H point. Similar studies by Bell and Owen on quenched Fe-N steels revealed no retained austenite below the H point.¹³⁾ These observations are in agreement with the proposed change in structure from the FCC to HCP to BCC transformation. All the C in solution in austenite is used up to form C-rich plates. At and above the H point, retained austenite is an important metastable phase in the martensitic structure. The amount of retained austenite increases with increase in C content with a wide range in values for a given C content. Tamaru and Sekito⁶³⁾ have shown that the amount of retained

Fig. 6 Influence of carbon on the amount of retained austenite in quenched Fe-C steels. The amount of retained austenite is negligible below the H-point. Above the H-point the data show large amounts of retained austenite that are influenced by processing history.

austenite increases with increase in temperature of quenching from 800 to 1000°C, and then decreases at higher temperatures. This influence of temperature of quenching on retained austenite has not been explained. Another variable is the quenching media that has been shown to be an important variable in determining the martensite-austenite ratio. Description of the hardening of steel objects described in ancient history include many colorful anecdotes on selection of the correct quenchant^{1,2)} and has been described as critical in achieving high hardness in the use of ancient steel objects. Subsequent processing after quenching such as cryogenic treating and mechanical deformation will decrease the amount of retained austenite. It will be shown that retained austenite is a major variable in interpreting the contribution of carbon-rich plates to properties of quenched Fe-C steels.

Figure 7 illustrates the influence of C on the hardness of quenched Fe-C steels. The data are taken from a number of investigators.^{47,52,67–70)} Dramatic differences in the hardness–C relation are observed below and above the H-point. The hardness increases monotonically with increase in C content from near 0 to 0.6 mass% C. In this region, the increase in hardness is directly related to the increase in number of C-rich phase particles with increase in C content and to the accompanying fine subgrain size. This structure is primary martensite. Upper and lower bounds are shown in the figure as solid and dashed lines respectively. The difference in strength below the H-point, which is influenced by different quenching conditions, has several possible origins. These are: (1) the size and spacing of the C-rich particles, (2) the composition of the particles, and (3) the subgrain size contribution. The hardness–C relation above the H-point, shown in Fig. 7, reveals an entirely different pattern. A wide range of hardness is observed. This variation is caused principally by the presence of two phases that are not very effective for strengthening, namely, the two solid solution phases, BCT phase and retained FCC austenite. The lower bound, given by the dash line contains the data of Sykes and

Fig. 7 Influence of C on the hardness of quenched Fe-C steels. The data of Kurdjumov, Irvine *et al.*, Kelly and Nutting, and Marder are documented by Krauss⁶⁾ and referenced in reference 67. The hardness-C relation below the H-point is related principally to the influence of C-rich phase and subgrains, and above the H-point principally to retained austenite and BCT martensite.

Jeffries⁶⁹⁾ in the as-quenched condition (1.0 mass% C, 1.23 mass% C and 1.59 mass% C). The continued decrease in hardness with increase in C content is attributed to the increase in retained austenite. Cryogenic treatment of the quenched 1.23 mass% C and 1.59 mass% C materials results in considerable increase in hardness. Further increase in hardness was achieved by room temperature tempering that allows precipitation to occur from the metastable BCT phase. Sunada *et al.*⁷⁰⁾ have shown that compression plastic deformation of their martensitic cryogenitic-treated steels (1.3 mass% C and 1.6 mass% C) achieved exceptional strengths. As an example, plastic straining increases the flow stress σ_y from 2.250 GPa to 4.351 GPa after 9% compression deformation for the 1.3 mass% C steel as a result of additional transformation of the remaining austenite. The flow stress of 4.351 GPa converted to Vickers hardness by $H_v = 2.5 \sigma_y^{71)}$ yields $H_v = 10.88$ and converted to DPH = 1090 (in units of kg/mm²). This high value is shown in Fig. 7. The continuous pattern of the maximum hardness for all C contents, both above and below the H-point, can be attributed to particle and subgrain/cell strengthening.⁷¹⁻⁷³⁾ Retained austenite and BCT martensite is no longer found in the structure.

4.6 Nature and composition of carbon-rich phases in quenched Fe-C steels

When an annealed Fe-C steel is heated to the austenite temperature range and then quenched it becomes less dense, i.e., of greater volume than in the original annealed condition. This was documented and known in 1722 when Reaumur, the

French renaissance-man and metallurgist, measured a volume increase of 2.1% after quenching a C steel of unspecified composition.⁷⁴⁾ He considered that this expansion, caused by a change in internal structure, was the clue to understanding the exceptional high strength of quenched Fe-C steels. His work led to a great improvement in the French steel industry for which he received a high prize. One can only share his enthusiasm when he stated that “we will not hesitate to include quench-hardening among the most wonderful phenomenon in nature”.

Subsequent researchers speculated on the change in internal structure. John Percy in his book published in 1864,⁷⁵⁾ considered that the formation of graphite particles, with its low density-large volume could explain the increase in volume upon quenching. In 1891, Howe in his book “The Metallurgy of Steel”⁷⁶⁾ proposed “hardinite” for the hard constituent discussed by Sorby.⁷⁷⁾ Howe proposed that hardinite was created not during quenching, but formed as a cluster of C and Fe atoms (akin to amorphous obsidian) prior to quenching, when heated to high temperature. Upon quenching this structure was frozen in and the result was hardinite and this could presumably lead to the Reaumur effect. This unusual model was revisited by Kaufman *et al.* and by Ansell *et al.*⁷⁸⁻⁸⁰⁾ In 1895, the name “martensite” was proposed for hardinite by the French metallurgist Osmond⁸¹⁾ to honor Martens, a German metallurgist who did metallographic studies on quenched high C steels.⁸²⁻⁸⁴⁾ The volume change from quenching in Fe-C steels is readily determined by density measurements. Nevertheless, it is a surprise that few systematic studies have been done on this property since the work of Reaumur. The work of Andrew *et al.* in 1925 is the only thorough study.⁶⁵⁾ The work has not been utilized in martensite studies and has only been briefly mentioned by Carpenter and Robertson in their book “Metals”.⁸⁵⁾ Andrew *et al.* showed that the volume was influenced by both C content and austenite transformation temperature, in the same way as studies on retained austenite that were done by Tamaru and Sekito (Fig. 6). The data of Andrew *et al.* will prove invaluable in the analyses that follow.

The additional volume generated by quenching must be explained by the creation of a new entity that has a bigger volume than Fe containing cementite. Good candidates are C-rich phases that have a larger volume (lower density) than cementite. Specific phases that fulfill this requirement are graphite, diamond, and the meta-stable carbides Fe_2C , Fe_7C_3 , and $\text{Fe}_{2.5}\text{C}$.³²⁻³⁴⁾ The densities of these phases are 2.25, 3.5, 6.7, 7.0 and 7.2 g/cc respectively. These densities, together with the known densities of cementite (7.66) and Fe (7.87), allow calculations of the volume of Fe containing particles for a given Fe-C steel.

Table 1 documents these calculations particularized for the maximum C content, 0.6 mass% C, that contributes to the formation of C-rich phases in hyper-H point composition Fe-C steels. The starting point begins with the first three columns, with the listing of the phases, their densities, and their specific volumes (reciprocal of the density). The next fourth and fifth columns are the steps that were used to calculate the volume fraction of C-rich phase (hereafter called particles, f_p) for each selected particle. Column 4 lists the percentage of atoms tied up in particles of different

Table 1 Calculation of specific volume of ferrite containing particles and volume fraction of particles in quenched Fe-0.60 mass% C (2.730 at% C).

Particle	Density ¹ , D , g/cc	Specific volume, $V_p = 1/D$, cc/g	Particles at%	Particles mass%	Particles vol%, f_p	Iron vol% $f_{Fe} = 100 - f_p$	$[V_{Fe+P}]_{comp}$ ² , cc/g
Graphite	2.20	0.45455	2.730	0.600	2.111	97.889	0.13397
Diamond	3.50	0.28571	2.730	0.600	1.337	98.663	0.12918
Fe ₂ C	6.70	0.14925	8.190	6.180	7.172	92.828	0.12865
Fe _{2.333} C	7.00	0.14286	9.100	7.109	7.913	92.087	0.12831
Fe _{2.5} C	7.20	0.13889	9.555	7.574	8.211	91.789	0.12803
Fe ₃ C	7.66	0.13055	10.920	8.969	9.182	90.818	0.12738
Fe	7.87	$V_{Fe} = 0.12706$					

Note 1: Densities of Fe_{2.5}C and Fe₂C were calculated by interpolation and extrapolation, respectively, from known densities of Fe_{2.333}C and Fe₃C.

Note 2: $[V_{Fe+P}]_{comp} = [V_{Fe+P}]_{Primary\ martensite} = f_p \cdot V_p + f_{Fe} \cdot V_{Fe}$.

stoichiometry assuming all C atoms are used up in forming the C-based particles. Column 5 converts the atomic percentage of column 4 to weight percentage. The results of the calculations for f_p are given in column 6. The next column gives the volume percent of the Fe matrix given by symbol $f_{Fe} = (100 - f_p)$. The end result is the prediction of the specific volume of the quenched Fe-C steel (column 8) calculated from the additive contribution of the specific volumes of the two components that make up the martensite structure in the Fe-0.6 mass% C material, namely pure α -Fe (V_{Fe}) and particles (V_p), as follows:

$$[V_{Fe+P}]_{Primary\ Martensite} = f_p \cdot V_p + f_{Fe} \cdot V_{Fe} \quad (1)$$

Equation (1) predicts the expected volume on quenching based only on the formation of particles. The equation is appropriate for C steels up to the H-point, i.e. 0.6 mass% C. The present authors used eq. (1) for analysis of the quenched Fe-C steels (0.22 to 0.5 mass% C) of Andrew *et al.*⁶⁵⁾ and Roberts *et al.*⁸⁶⁾ The result is plotted as data points in Fig. 6 showing no retained austenite since the volume changes were fulfilled by the creation of carbide particles.

For C steels above the H-point, account must be taken of additional structural changes involving the presence of the BCT phase in primary and secondary martensite and of retained austenite. The volume of the quenched composite structure (V_{comp} in Fig. 5(b)) is described by the following relation:

$$V_{comp.} = f_\gamma \cdot V_\gamma + (1 - f_\gamma) \cdot V_{M.P.} \quad (2)$$

Equation (2) is the basis for analyzing the 0.88 mass% C steel and for determining the composition of the particle responsible for the volume increase from quenching. The first term is the volume fraction of retained austenite (f_γ) times the specific volume of retained austenite (V_γ). The second term is the volume fraction of martensite times $V_{M.P.}$ that represents the volume of martensite products from primary and secondary martensite. It was described in Fig. 4 that primary martensite consists of the creation of two different phases. One is related to the volume created from transformation to form the BCC phase containing C-based plates, and the other to form the enriched BCT phase, as follows:

$$V_{primary\ martensite} = a[V_{BCC+P}]_{0.6\ mass\% C} + b[V_{BCT}]_{c\ mass\% C} \quad (3)$$

In eq. (3) the constants 'a' and 'b' are taken as the weight fraction contributions to forming BCC + P (particles) and enriched BCT phases respectively. The constant 'c' is the composition of the enriched BCT phase. The values of a , b , and c for the 0.88 mass% C steel are 0.68, 0.32, and 1.475 respectively. Once primary martensite transformation is completed, secondary martensite begins to form. The later transformation involves a relatively simple process. It is the Bain transformation, involving only a compression strain to create the BCT phase. The total volume that is created to form the martensite product, ($V_{M.P.}$) for the 0.88 mass% C steel, is described as follows:

$$V_{M.P.} = A \cdot \{a[V_{BCC+P}]_{0.6\ mass\% C} + b[V_{BCT}]_{1.475\ mass\% C}\} + B[V_{BCT}]_{0.88\ mass\% C} \quad (4)$$

The terms A and B are the relative volume fractions of primary and secondary martensite respectively. In the case of the 0.88 mass% C steel the values of A and B are estimated from the ratio of the temperature range of primary martensite formation (725–220°C) and secondary martensite formation (220–20°C) to the total temperature of transformation. The calculated values are $A = 0.716$ and $B = 0.284$.

The nature and composition of the particle, $[V_{BCC+P}]_{0.6\ mass\% C}$ for the case of the 0.88 mass% C steel is predicted by combining eqs. (2) and (4) to yield:

$$[V_{BCC+P}]_{0.6\% C} = (1/Aa)\{(V_{comp} - f_\gamma V_\gamma)/(1 - f_\gamma)\} - Ab[V_{BCT}]_{1.475\% C} - B[V_{BCT}]_{0.88\% C} \quad (5)$$

Calculation of the volume of the BCC phase containing particles requires obtaining values of $V_{comp.}$ and f_γ for the 0.88 mass% C steel. The archival work of Andrew *et al.* on density studies in 1925 and of Tamaru and Sekito in 1931 on retained austenite provides this information. In both cases the authors recorded the results of samples quenched from different temperatures in the austenite range. Table 2 documents these values. Calculation of specific volume of the particle from eq. (5) requires knowledge of the specific volumes of V_γ and V_{BCT} at 0.88 mass% C and V_{BCT} at 1.475 mass% C. These are 0.12419 cc/g, 0.12999 cc/g, and 0.13208 cc/g respectively taken from the X-ray summary work of Cheng *et al.*¹⁹⁾ The calculated values of $[V_{BCC+P}]$ through eq. (5) are summarized in the last column of

Table 2 Calculation of $V_{\text{BCC+P}0.60\text{ mass\% C}}$ from eq. (5).

Quenching Temperature (°C)	Vol. Quenched Composite Structure (V_{comp} , 1/D (cc/g)), from Andrew <i>et al.</i> @0.9 mass% C	Volume fraction retained austenite (f_{γ}), from Tamaru and Sekito @0.88 mass% C	$V_{\text{BCC+P}0.60\text{ mass\% C}}$ Predicted by eq. (5) (cc/g)
800	0.12852	0.108	0.12707
900	0.12891	0.175	0.12886
1000	0.12895	0.192	0.12919
1100	0.12895	0.180	0.12902

Constants for eq. (5):

$$a = 0.68, b = 0.32, A = 0.716, B = 0.284,$$

$$V_{\gamma} = 0.12419 \text{ cc/g}, V_{\text{BCT}0.88\text{C}} = 0.12999 \text{ cc/g}, V_{\text{BCT}1.475\text{C}} = 0.13208 \text{ cc/g}$$

$V_{\text{BCC+P}} @0.60\text{ mass\% C}$, from Table 1 (cc/g)					
Graphite	Diamond	Fe ₂ C	Fe _{2.333} C	Fe _{2.5} C	Fe ₃ C
0.13397	0.12918	0.12865	0.12831	0.12803	0.12738

Table 2. A comparison is made between the calculated values and those deduced for the five candidates for particles given in Table 1 and repeated in Table 2. The prediction is that the likely particle created in martensite by quenching from 1000 and 1100°C is diamond, whereas it is close to η carbide (Fe₂C) by quenching from 900°C. The particle predicted by quenching from 800°C had an even smaller specific volume than that predicted for cementite and may be attributed to incomplete dissolution of C in austenite at this low temperature. The creation of diamond particles was speculated by the present authors in previous publications,^{11,71} where it was noted that diamond and Fe are in equilibrium at low temperature.^{87–89} The described model is based on the formation of an enriched BCT phase from quenching. In the model given in Fig. 4B, it was shown that enriched FCC could have been retained in the final quenched martensite structure as the most stable phase. A calculation was made using eq. (5) for the case of enriched FCC phase. The calculation involved substituting $[V_{\text{BCT}}]_{1.475\text{C}} = 0.13208 \text{ cc/g}$ with $[V_{\text{FCC}}]_{1.475\text{C}} = 0.12792 \text{ cc/g}$. The result yields a higher value of the predicted volume of the carbon-rich phase by an amount $\Delta = 0.00196 \text{ cc/g}$. The new prediction indicates the creation of the diamond phase for the specimen quenched from 800°C, and even lighter than diamond for the higher austenitizing temperatures. The new calculation predicts a specific volume for the carbon-rich phase, for all quenching temperatures (except 800°C), that is greater than the specific volume of diamond. This result suggests that some of the enriched FCC does transform to enriched BCT but diamond is believed to be the most likely carbon-rich phase.

A brief history of diamonds and steel is worth describing. Ferdinand Frederic Moissan (Henri) invented the electric arc furnace, and was claimed to be the first to synthesis diamond from an Fe-C alloy. In 1893, he did what would now be called a splat quenching type experiment. He dissolved charcoal in molten iron up to 3500°F (in his furnace) and then quenched the molten mass into water. Upon dissolving the solidified steel in hydrochloric acid, he claimed to have found microscopic particles of diamond. Other researchers repeated his experiment apparently without achieving

success. Moissan was also known for discovering the element fluorine, for which he was awarded the 1906 Nobel Prize in Chemistry. In the modern splat quenching experiments of Cadeville *et al.*⁴² the authors' analyses by X-rays also predicted the formation of particles (but as cementite). Subsequent electron microscopy studies, however, did not reveal particles.⁴² Sauveur in his book on metallurgical reminiscences⁹⁰ considered that particles, of sub-microscope size, formed during quenching of Fe-C steels. Sauveur was also known to be an avid proponent of the concept that an HCP type phase of Fe was important in the transformation process of Fe-C steels during quenching. He considered that this phase, named β , was akin to the paramagnetic BCC phase of Fe that exists from 760 to 910°C.

The particles that are created by quenching are expected to have a size representative of embryonic-nucleation. Zhao *et al.*⁹¹ have calculated, thermodynamically, that the minimum size for nucleation of particles in Fe is 1 nm. The embryonic particle size can be expected to be the same size irrespective of C content. When particles are in the size range of one nanometer, it may be possible they can be viewed as a cluster of C and Fe atoms. Mossbauer studies^{42,92} indicate the existence of clusters of C in Fe. How clusters may contribute to understanding density and strength changes in Fe-C steels seems not to have been explored.

5. Summary and Conclusions

The scientific literature contains a number of experimental and theoretical studies that provide insight into the martensitic transformation in quenched Fe-C steels. Many of these studies, spanning over 100 years of work, however, contain data and observations that were not resolved by the models prevailing at that time. For example, structural changes known to occur prior to the M_s have been observed but not explained. In addition significance changes in structure and properties of quenched martensite at 0.6 mass% C are known but not explained. Noteworthy is the absence of BCT structure in the C range below 0.6 mass% C.

The present manuscript proposes a model of martensite formation that addresses many of the unexplained observa-

tions. The model is based on the formation of a primary and secondary martensite. Below 0.6 mass% C only primary martensite is created as BCC iron plus a carbon-rich phase. Above 0.6 mass% C, both primary and secondary martensite are created with secondary martensite appearing as the traditional BCT plates adjoining retained austenite. The following conclusions are derived from the model and subsequent analysis regarding the structure of martensite:

- (1) The constant value of $c/a = 1$ for C concentrations from 0 to 0.6 mass% is interpreted as evidence for the formation of martensite with a BCC structure, containing a meta-stable C-rich phase (P). The transformation is designated as primary martensite and follows the sequence FCC $\rightarrow$ HCP and HCP $\rightarrow$ BCC + P.
- (2) The discontinuity at 0.6 mass% C (the H point) is explained as the limit of solubility of C in the HCP phase of Fe during transformation.
- (3) The primary martensite structure created above 0.6 mass% C contains a mixture of C-rich phase in BCC iron with a BCT phase that is richer in carbon than the parent composition. The transformation is described as FCC $\rightarrow$ HCP + enriched FCC followed by HCP + enriched FCC $\rightarrow$ BCC + P + enriched BCT.
- (4) Secondary martensite is acicular plate martensite, consisting of a mixture of two meta-stable solid solution phases, the BCT phase and retained austenite.
- (5) The model predicts the specific C-rich phase that forms in a quenched 0.88 mass% C steel, and is identified either as diamond or Fe₂C.

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