

The iron-carbon phase diagram for the solid state

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Abstract

The part of the binary Fe-C phase diagram that deals with the solid state is an impressive manifestation of the complexity of pure-iron and the consequences of carbon additions. Its origins reveal a story that inspires today, how ferromagnetism caused confusion, and yet stabilises the most important phase in the microstructure of colossal quantities of structural steels. There are unresolved issues – if graphite is ignored, is the stable phase field at ambient temperature defined by a mixture of cementite and ferrite? Some studies favour mixtures of iron carbides (χ , η , ϵ) and ferrite to represent equilibrium at low temperatures, but it is shown that this may not be correct. Should we limit ourselves to the body-centred cubic form of ferrite when interpreting equilibrium, or does the stability of mixtures of body-centred tetragonal ferrite and austenite take precedence when the lattice change is generated by the Bain deformation? A case is made for the routine inclusion of the T_0 curve on the phase diagram, on the basis that it is no different in its thermodynamic definition from the equilibrium phase boundaries of pure iron in a pressure-temperature plot.

1 Introduction

The Fe-C phase diagram is essential even though *all* steels contain additional solutes, because it serves as the fundamental base map for almost all steel metallurgy. It provides the core framework for understanding, estimating, and attempting to logically control the structures of commercial alloys. The diagram is a revealed truth over historical time-scales, reflecting the complexity of the material even in its binary form. It is incredible that the first discovery of solid-state transformations in steel, began with the visual observation of huge objects.

Dmitry Konstantinovich Tschernoff, born in Petrograd during 1839, joined the Oboukoff iron works in 1866, where ‘he trained his eye to gauge correctly the temperatures of cooling billets’

[1]. He thus made the discovery of the critical temperatures of steel, as explained by his student Colonel N. T. Belaiew [2]. Tschernoff in his experiments did more – witness the remarkable image in Figure 1 showing large iron crystals isolated from a casting, in an era where crystal growth involved suspending a seed from a string into a supersaturated solution. Incidentally, Belaiew was thoroughly familiar with the work of Sorby, the first to study the ‘microscopical structure of iron and steel in order, if possible, to throw light on the origin of meteoric iron’ [3].

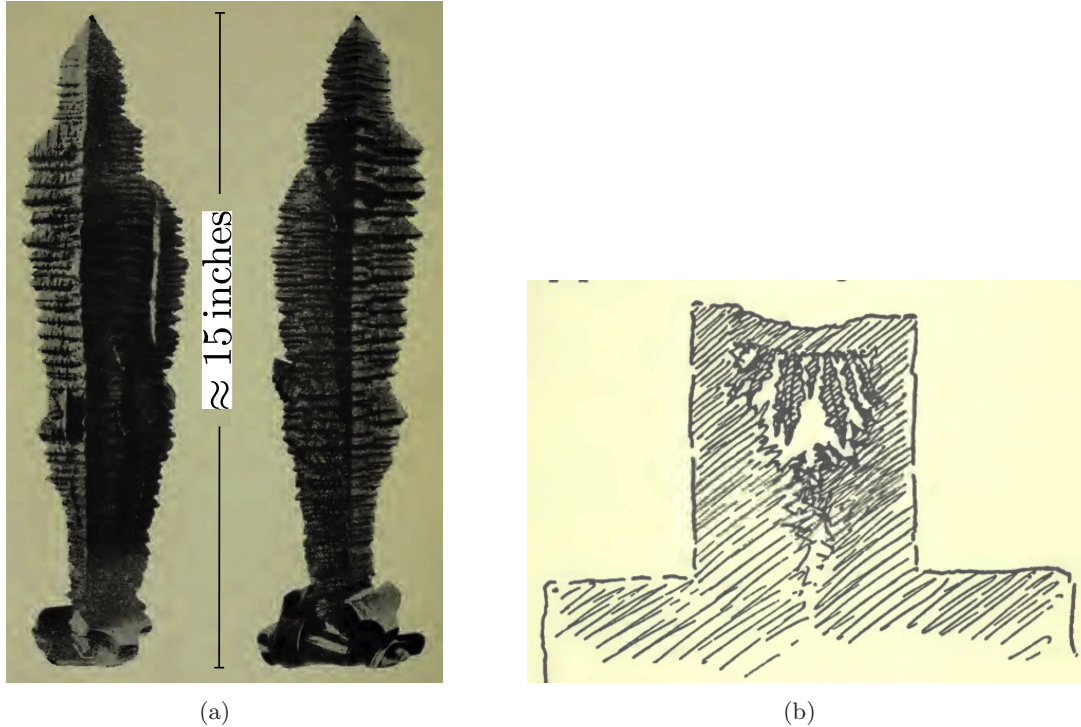


Figure 1: Fe-0.6C wt% steel. (a) Iron crystals, about 15 inches in length, isolated from a casting. The crystals were recognised to grow fastest normal to the temperature gradient. (b) The crystals formed in a cavity of a casting. Image and drawing after Tschernoff, published by his student Belaiew, who himself made extraordinary contributions to steel metallurgy [4]. Colonel Belaiew in 1907-1908 had a number of steels prepared at the steel works ‘under conditions of extreme slowness of cooling’, aiming to bring ‘into closer harmony the processes of crystallisation with various areas of the equilibrium diagram’ [3].

Tschernoff’s work was announced to the Imperial Russian Technical Society and became internationally renowned, translated and honoured. Floris Osmond then conducted thermal analysis experiments that defined the terminology for the transformation points during cooling (i.e., *refroidissement* Ar_i where the subscript refers to a particular transformation) and heating (*chauffage* Ac_i) [5], at a time when the allotropic forms of iron were not well defined, nor whether they were amorphous or crystalline – the Bragg equation for X-ray diffraction was published in 1913 [6]. The thermal studies form the basis of the equilibrium transformation temperatures now known as Ae_3 and Ae_1 in the modern equilibrium Fe-C phase diagram, with the missing Ae_2 representing the ferromagnetic $\rightleftharpoons$ paramagnetic transformation in ferrite (α). For an appropriate steel, Ae_1 is the

temperature at or below which pearlite can form. Osmond and Wearth [7] refer to Tschernoff on several occasions in their later paper.

Belaiew had hoped to build on Sorby’s work, by slow cooling steels in order see pearlite with the naked eye, rather as the contemporary observations of meteorite structures. Alas, the prospect of sufficiently coarse pearlite ‘still seemed very distant’ [8], not surprising in hindsight, given that meteorites cool at $1\text{-}1000\text{ K Myr}^{-1}$ [9].¹ But the studies led to some remarkable insights: that the pearlite proceeds with a certain constant velocity, that it only can form if the alloy is supersaturated simultaneously with regard to both components (it is common to refer to this as the Hultgren extrapolation on the Fe-C diagram, but Belaiew was much earlier). He may have been the first to deal with the ‘stereometry of the pearlite grain’, when he wondered why the interlamellar spacings varied across the field of observation – he worked out correctly that the plane of section matters. He further considered the case where the true interlamellar spacing may not be uniform. Regrettably, modern instrumentation is so easy to use, that there are countless papers published with no thought given to stereology in plotting distributions based on two-dimensional sections, Figure 2. A random section will rarely intersect the exact centre of a grain. Therefore, the two-dimensional distribution will result in a size smaller than the true size of the grain. In the case of mono-dispersed spheres, the mean diameter perceived from two-dimensional sections will be $\pi/4$ of the true diameter [11]. But for space-filling shapes such as grains, shape and orientation also feature in the calculations.

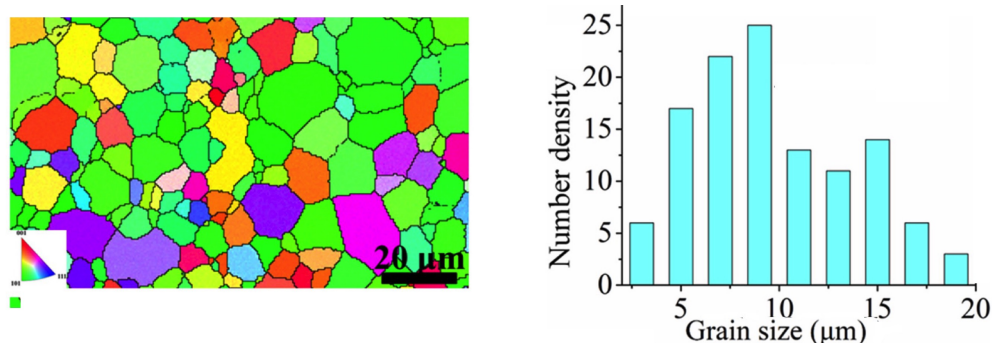


Figure 2: An alleged measured grain size distribution that does not account for stereological factors, published during 2025 [12]. The ‘grain sizes’ in the distribution on the right really represent *apparent* sizes, not true dimensions. Images reproduced and adapted under the Creative Commons CC-BY license.

Some of the older phase diagrams identify phase fields containing mixtures of pearlite (P) and proeutectoid ferrite, instead of a two-phase field of α +cementite (θ), Figure 3. Pearlite is an important constituent of many structural steels [10]. Its explicit identification on the phase diagram may have given the impression that the lever rule can be used to estimate the fraction of pearlite, when one end of the lever is at the eutectoid composition. The origin of the term *eutectoid* is interesting. During 1888, Henry Marion Howe first described the constituents of steels as pearlite, ferrite and cementite [13]. He felt uneasy referring to pearlite as eutectic, because a eutectic implies

¹The coarsest pearlite ever created has an interlamellar spacing of $\approx 0.5\text{ mm}$, fabricated by Minoru Umemoto and his team at Toyohashi University, by artificially bonding alternating layers of cementite and ferrite [p.331, 10].

a lowest melting point. In a letter to Sauveur on the 4th of June 1903, he wrote [14]:

Let us use the word ‘eutectoid’ to denote alloys of lowest transformation point. The suffix ‘oid’ clearly indicates that the eutectoid has the form of other important properties of the eutectic; it keeps the resemblance of the eutectoid to a eutectic before the mind, while it allows us to preserve the initial meaning for eutectic and to distinguish between these two really distinct though related entities.

The carbon concentration of the eutectoid point often was set in the range 0.9-0.92C wt% [15–18] in books and publications extending to beyond 1944. The eutectoid temperature itself was set as low as 700 °C [p. 107, 18]. The carbon content of cementite itself was in 1878 measured chemically to be in the range 6.01-7.38 wt% [19] with later (1883) it to approximate ‘the formula Fe_3C or to a multiple of that formula’.

Figure 3 also shows a phase field containing β -iron which is absent from all modern phase diagrams, because the Curie transition in α -iron was associated erroneously with the $\beta \rightarrow \alpha$ transition. We shall see later that we now know that there is a perceptible change in symmetry of the α at the point of the paramagnetic $\rightarrow$ ferromagnetic transition.

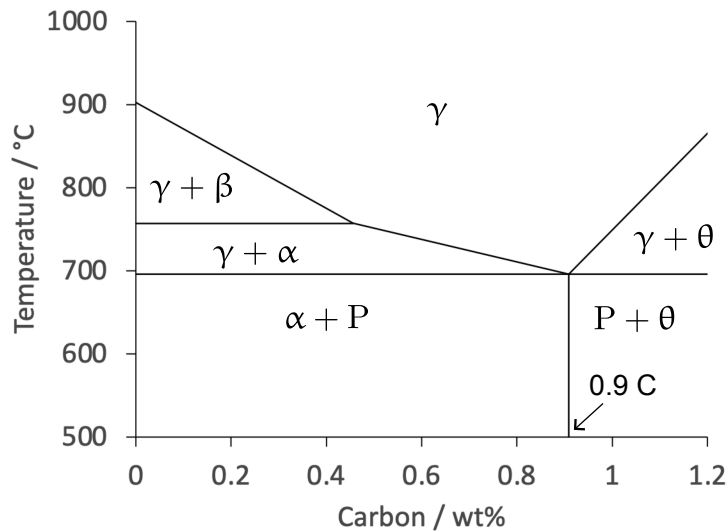


Figure 3: A selected part of Rosenhain’s Fe-C equilibrium phase diagram as known in 1911 with annotation added. γ , α , θ and P represent austenite, ferrite, cementite and pearlite, respectively. At the time, the Curie transition was associated with a $\beta \rightarrow \alpha$ allotropic transformation with the β phase being much harder than α ; quenching the steel was supposed to retain the β and hence to harden the steel. The eutectoid composition was set approximately at 0.9 wt% carbon, with the eutectoid temperature somewhat below 700 °C. The α and β single-phase fields are missing.

2 Solid phases in the Fe-C diagram

These are listed in Table 1; ferrite is the predominant phase present in some 2 billion tonnes of steel consumed annually. It would not exist at all under ambient conditions were it not for its ferromagnetic state. Hexagonal close-packed ϵ -iron would replace α -iron [20], resulting in all the difficulties associated with the reduced symmetry of the ϵ -lattice. It is not an exaggeration to suggest that modern civilisation would not be possible without the ferromagnetic state of ferrite. Actually, even austenite has a peculiar magnetic structure with its low- and high-spin states, that manifests in ordinary life as a thermal expansion coefficient that much exceeds that of ferrite, making austenitic steels inappropriate for power plant applications where large fluctuations of temperature cause thermal fatigue [pp.30-38, 21].

Graphite in contact with ferrite has a smaller free energy than a mixture of cementite and ferrite. Figure 4a shows a modern phase diagram, calculated using thoroughly assessed thermodynamic data, where the red curves represent the iron-graphite version. Graphite generally is too slow to form in ordinary steels, largely because of the difficulty of nucleating the phase. It seems that the first carbon to grow from the cementite is amorphous so the interfacial energy during nucleation must be very large. But graphite precipitation from cementite requires the presence of ferrite; Figure 5 shows that in the absence of ferrite, cementite remains more stable than graphite, but this reverses when ferrite is permitted to coexist with the cementite.

Table 1: Phases participating in the Fe-C equilibrium phase diagram for ambient pressure. The transition carbides χ and η are listed here because some calculations identify them to be in equilibrium with α in preference to cementite under circumstances discussed in the text.

Phase	Symbol	Space group	Comment
Ferrite	α	$Im\bar{3}m$	Paramagnetic $T > T_C$
Ferrite	δ	$Im\bar{3}m$	$\equiv \alpha$, historical duplication
Ferrite	α	$I4/m\bar{m}'m'$	Ferromagnetic $T < T_C \approx 1042$ K
Austenite	γ	$Fm\bar{3}m$	
Cementite	θ	$Pnma$	Ferromagnetic $T < T_C \approx 459$ K
Hägg-carbide Fe_5C_2	χ	$C2/c$	Ferromagnetic $T < T_C \approx 525$ K
Fe_2C	η	$Pnnm$	Ferromagnetic $T < T_C \approx 540$ K
Graphite	G	$P6_3/mmc$	$R\bar{3}m$

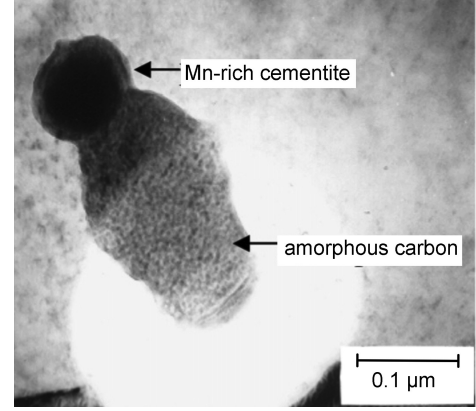
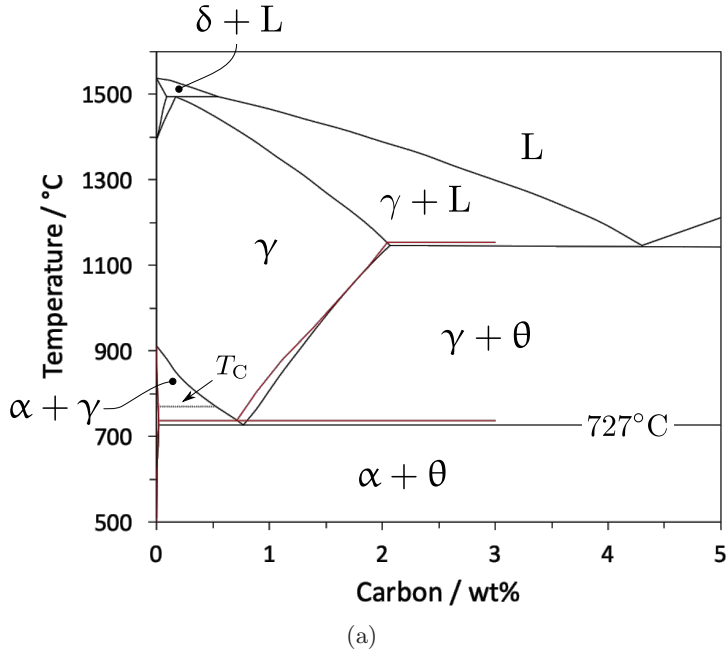


Figure 4: (a) The iron-carbon equilibrium phase diagram, in part calculated using assessed thermodynamic data. T_C represents the Curie temperature of ferrite, θ the cementite and L the liquid phase. The more stable equilibrium between the allotropic forms of iron and graphite is represented by the red lines. However, graphite may not actually form due to kinetic limitations. Some equilibrium microstructures are illustrated in [22]. (b) Fe-0.38C-1.82Si-1.44Al-0.07Mn wt%, annealed at 680 °C for 58 min, showing amorphous carbon nucleated from a cementite particle. Image reproduced from [23] with permission of Elsevier.

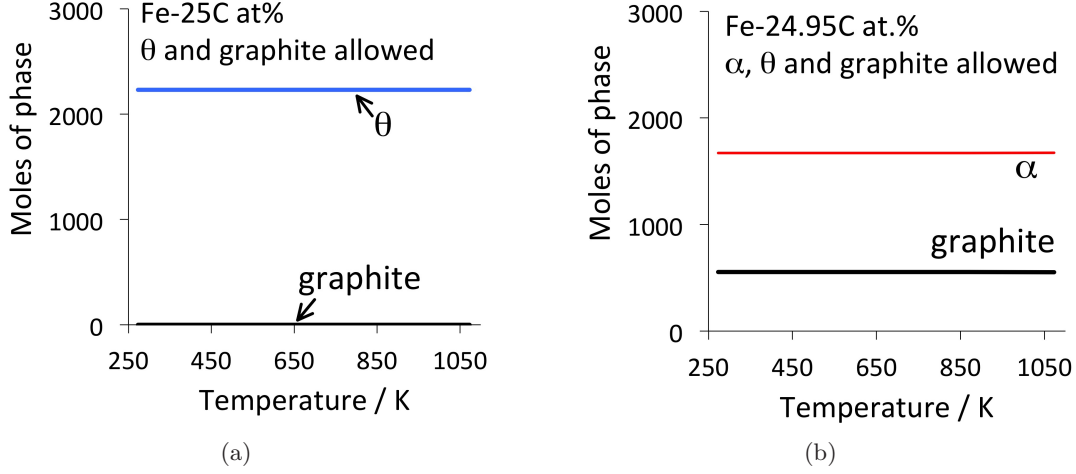


Figure 5: Phase diagram calculations for 100 kg total weight, using MTDATA [24] and the SGTE thermodynamic database. (a) Fe-25C at.%, permitting only cementite and graphite to co-exist. (b) The average carbon concentration is reduced slightly to allow ferrite to appear, in which case the most stable mixture becomes that of ferrite and graphite [25].

3 T_0 curve routinely on the phase diagram?

In the phase diagram for *pure* iron as a function of both temperature and pressure, there are domains representing combinations of $\{P, T\}$ where the solid phases α , γ , ϵ and liquid iron are stable. Curves such as ‘ab’ on Figure 6a, that separate a pair of phases such as γ and α , represent the locus of points where their free energies are identical $G_\gamma = G_\alpha$ and where they can coexist at equilibrium.

The T_0 curve in Fe-C or Fe-C-X, where ‘X’ represents a substitutional solute, also represents the case where α and γ of the same chemical composition have the same Gibbs free energy. Given its enormous technological consequence, it may be timely to include a T_0 curve, i.e., the locus of all points where $G_\gamma = G_\alpha$ when $x_C^\gamma = x_C^\alpha$, on the temperature versus carbon concentration equilibrium phase diagram. One might argue that the T_0 curve does not represent equilibrium in the same way as curve ab in Figure 6a. However, the boundaries illustrated in Figure 6a are not sacrosanct. They would shift if, for example, a large magnetic field is imposed at $T < T_C^\alpha$ because the stability of α relative to γ would change. In the case of the T_0 curve, allowing atomic mobility would undoubtedly lead to a lower energy state, but the definition of T_0 is identical to that of the curves on the pure-iron phase diagram. Indeed, on the Fe-C phase diagram, the T_0 curve begins at exactly the same temperature as the $\alpha \rightleftharpoons \gamma$ transition when the carbon concentration is zero, Figure 6b.

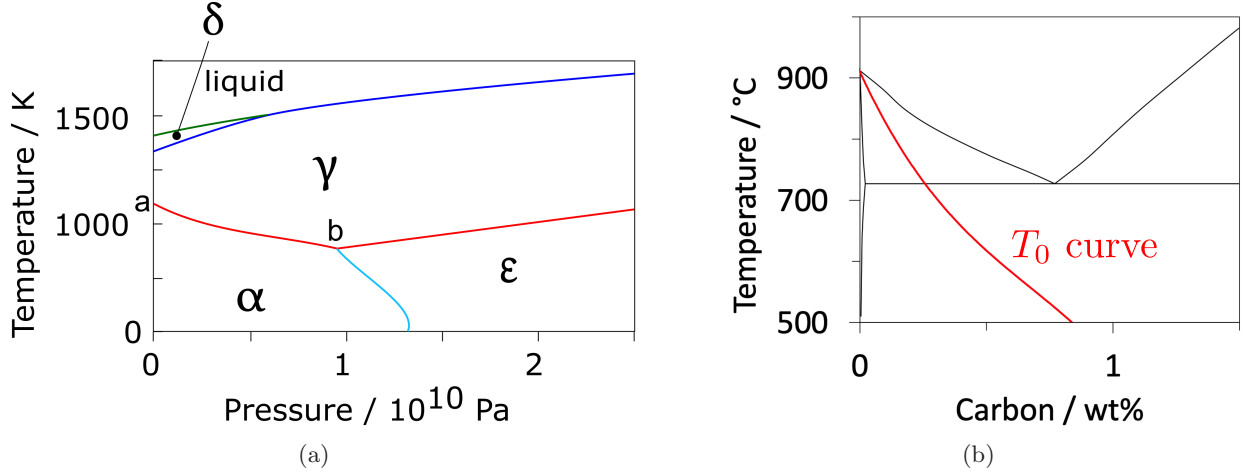
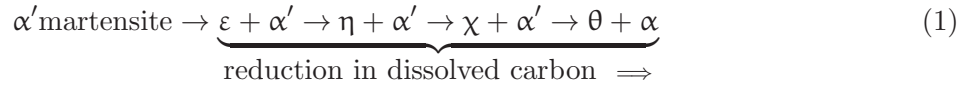


Figure 6: (a) Temperature versus pressure equilibrium phase diagram for pure iron, based on assessed thermodynamic data. α , γ and ϵ refer to ferrite, austenite and ϵ -iron respectively. δ is simply the higher temperature designation of α . Diagram courtesy of Shaumik Lenka, calculated using the database ‘TCFE8’, and ThermoCalc version 2015b. (b) The low-temperature part of the Fe-C phase diagram including the red T_0 curve. The other phase fields are as in Figure 4.

4 Transition carbides or not?

The conventional wisdom of the sequence of precipitation reactions that occur during the tempering of martensite in steels is as follows [26, 27]:



where α' refers to martensite and α to ferrite. This implies that the first three iron-carbides in this equation form only because there is some kinetic advantage over the more stable cementite.

Chipman [28, 29] first contradicted this picture, by suggesting that there is a phase field in the Fe-C equilibrium diagram, where mixtures of χ -carbide and ferrite may be more stable than those of cementite and ferrite, even at the smallest of carbon concentrations. The data utilised to reach this conclusion were based on experiments in which iron was reacted with butane [30]. Based on a single point from these experiments, Chipman derived an admittedly approximate equation for the free energy of formation of χ from α -Fe and graphite, in order to define the $\chi + \alpha$ phase field on the Fe-C diagram. Given the uncertainties in the data, he emphasised the need to distinguish thermodynamic and kinetic effects, i.e., whether the experiments on the relative stabilities of χ and θ are sufficiently long to achieve equilibrium.

Naraghi et al. [31] represented the thermodynamic data for χ and η using data for cementite, but weighted by the composition, for example, by writing the heat capacity at constant pressure as $C_P^\chi = \frac{5}{3}C_P^\theta + \frac{1}{3}C_P^{\text{graphite}}$. They did not publish the Fe-C phase diagram for temperatures below 900 K,

but provided us with the necessary assessed data, resulting in the diagram illustrated in Fig. 7. The clear implication is that that χ and η are not always *transition* carbides. The extraordinary outcome is that if a mixture of $\theta + \alpha$ is cooled, the cementite would be replaced by χ and eventually, η – the reason why this has never been observed could be kinetic. The purpose of the work presented here was to assess whether such a diagram is viable.

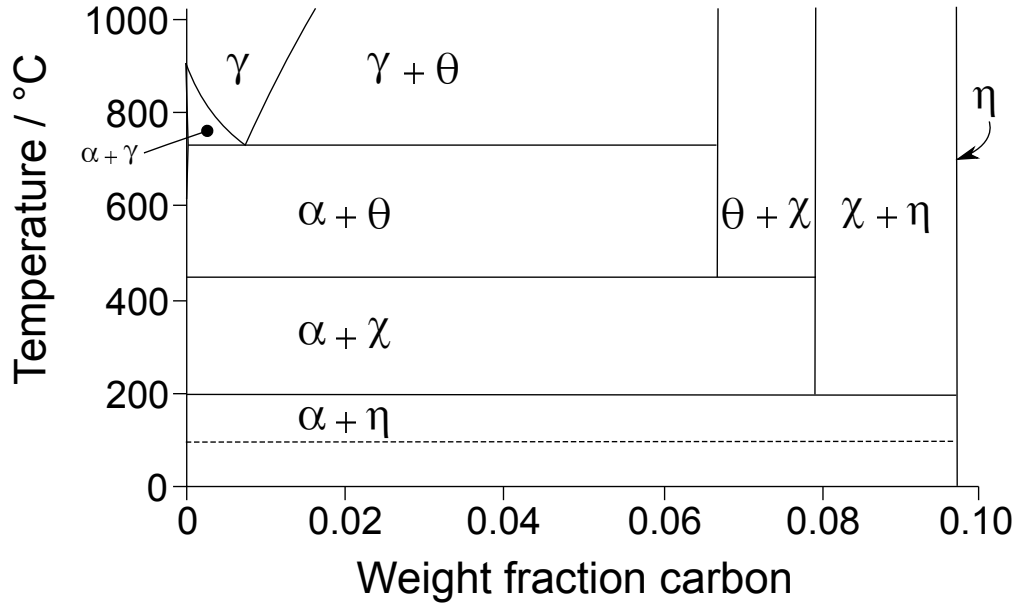


Figure 7: Part of the iron-carbon equilibrium phase diagram calculated using data provided by Naraghi et al. [31]. The dashed line represents a temperature below which a solid solution of iron and carbon may tend to undergo the clustering of carbon atoms as a precursor to a conditional spinodal.

Figure 8 summarises a compilation of data on Fe-C steels in which iron carbides precipitate either from supersaturated-ferritic or during the tempering of martensite. A Larson-Miller parameter [32] is used to represent empirically, the combined effect of time and temperature of the heat treatment. Cementite is seen to be the most stable phase over a wide temperature range when the strength of the heat treatment is greatest. Secondly, that cementite is the only precipitate when the excess carbon concentration is small. This is expected because a small carbon concentration corresponds to a small driving force for precipitation, in which case metastable precipitates cannot form spontaneously.

An investigation of literature data and our own experiments establish that it is not correct to identify a $\chi + \alpha$ phase field on the iron-carbon equilibrium phase diagram (Fig. 7), one which is supposed to be more stable than $\theta + \alpha$. Analysis of the published data indicates that the $\eta + \alpha$ phase field on Fig. 7 is also unlikely to be correct because only cementite is observed to form in very low carbon steels at low tempering temperatures. The conclusion is that the thermodynamic data on which the phase diagram calculations are based need further probing.

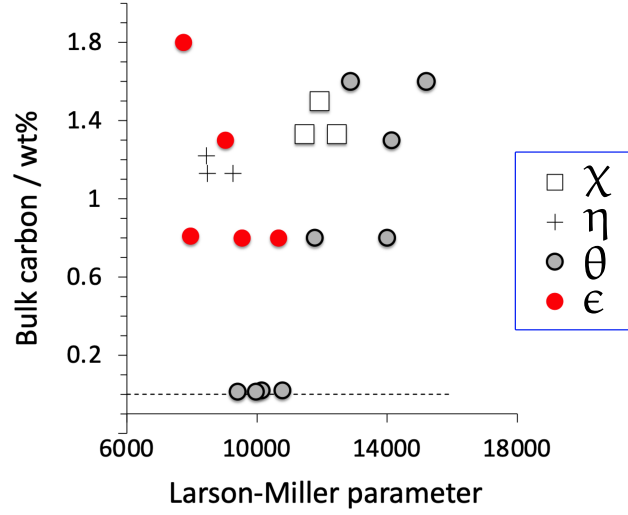
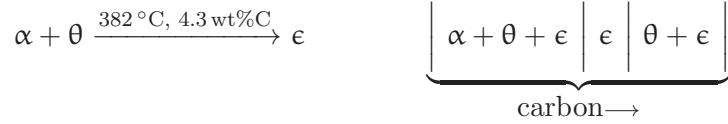


Figure 8: Plot of data on Fe-C alloys against a Larson-Miller parameter $T(\log t + 20)$, where T is the absolute tempering-temperature and t the tempering time in hours. The new data describe cementite obtained from our own tempering experiments as described below. Data compiled from [33–38, 38–43].

Davydov [44] has proposed a peritectoid reaction,



with $\alpha + \theta + \epsilon$ and $\theta + \epsilon$ equilibrium phase-fields on either side of a narrow ϵ phase field for $T < 382^\circ\text{C}$. To the author’s knowledge, there is no credible evidence to support this.

5 Vestiges

The first stage, the plate that forms without any change in composition, is the most difficult to isolate, but there are extraordinary vestiges of this initial event that prove the mechanism. Atom probe investigations have always revealed carbon concentrations in bainitic ferrite that are far in excess of equilibrium concentrations, thought originally to be located at dislocations [45–55]. The first observation using methods where the concentration can be measured in defect-free solid solution was by Pereloma et al. [56], followed shortly afterwards by Caballero et al. [57, 58]. The concentrations observed are far greater than expected from equilibrium. Figure 9a shows data from an atom probe experiment, collected from regions that are free from defects. Although the measured concentrations are less than $\bar{x}$, they are much greater than expected from equilibrium. The excess carbon persists in the ferrite even after holding at the transformation temperature of

200 °C for 250 h, so it is not the mobility of the carbon that prevents it from partitioning into the residual austenite.

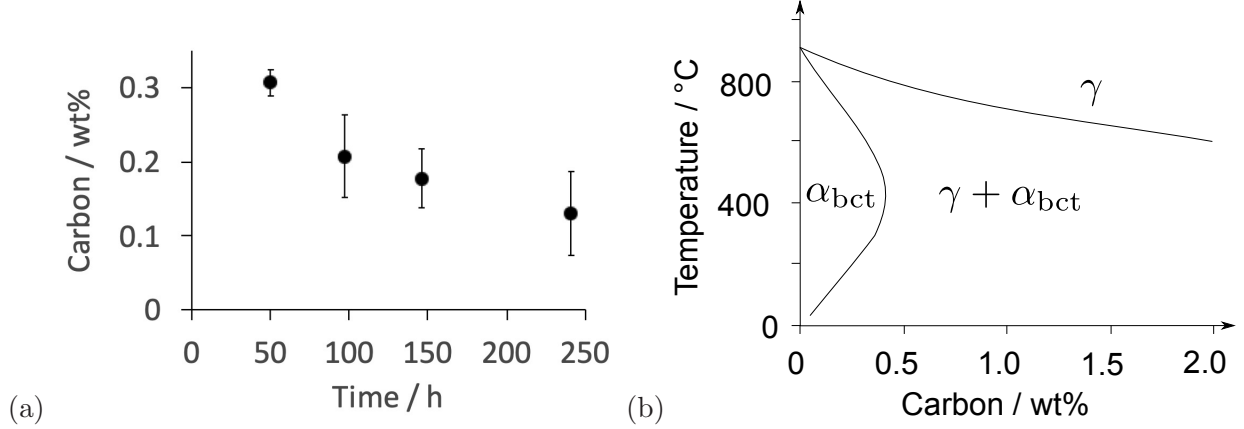


Figure 9: (a) Carbon concentration in solid solution within bainitic ferrite as a function of transformation time at 200 °C, Fe-1C-1.5Si-1.9Mn-1.3Cr-0.26Mo wt%. Adapted from Garcia-Mateo et al. [59]. (b) Calculated phase diagram for the equilibrium between body-centred tetragonal ferrite and austenite. After Jang et al. [60].

The reluctance of the carbon to partition from α_b is because the Bain strain leaves the carbon atoms inherited by the α_b on one sub-lattice of the interstices, making the unit cell tetragonal in the first instance; the tetragonal cell of bainite has been verified experimentally using a number of techniques [59, 61–66]. As a consequence, the equilibrium to be considered is between the body-centred tetragonal ferrite (α_{bct}) and austenite, not that between bcc-ferrite and austenite. Figure 9b shows a calculated Fe-C diagram for the α_{bct}/γ equilibrium [60]; it is evident that the solubility of carbon is increased significantly relative to bcc-ferrite.

6 Conclusions

1. The idea that an $\alpha + \theta$ mixture is less stable at $T \lesssim 430\text{ K}$ than $\alpha + \chi$ or $\alpha + \eta$ does not fit experimental observations. These iron-carbides are properly regarded as transition states that morph into cementite during annealing.
2. The T_0 curve along which austenite and ferrite of identical composition have the same free energy is of considerable technological importance. A case is made for its routine incorporation in the Fe-C phase diagram, given that its thermodynamic definition is identical to the phase boundaries between the allotropic forms of pure pure substances.
3. The unexpected retention of excess carbon in supersaturated ferrite that is in contact with austenite at temperatures where it is mobile, may be explained by considering the equilibrium between tetragonal ferrite and austenite.

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