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Carbon partitioning into austenite after martensite transformation

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Abstract

A model is developed to describe the endpoint of carbon partitioning between quenched martensite and retained austenite, in the absence of carbide formation. The model assumes a stationary α/γ interface, and requires a uniform chemical potential for carbon, but not iron, in the two phases, leading to a metastable equilibrium condition identified here as “constrained paraequilibrium” or CPE. The model is explained with example calculations showing the characteristics of the constrained paraequilibrium condition, and applications are discussed with respect to new microstructures and processes, including a new “quenching and partitioning,” or Q&P process, to create mixtures of carbon-depleted martensite, and carbon-enriched retained austenite. Important new implications with respect to fundamental elements of the bainite transformation are also discussed.

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1. Introduction

Carbon partitioning between ferrite and austenite during high temperature diffusional transformations is relatively well understood. These reactions are frequently referred to as reconstructive transformations, because of the short-range diffusional movements of iron (and substitutional) atoms that accomplish a change in crystal structure between bcc and fcc [1]. In contrast, the details of carbon partitioning during or after displacive or martensitic transformations are somewhat more

controversial, particularly with respect to the growth of bainite. In martensite, the displacive transformation (i.e. a process that involves coordinated rather than diffusional movements of the iron atoms) is usually believed to occur without diffusion of carbon or other interstitials [2], and thus the body-centered martensite phase can be substantially supersaturated with carbon. Subsequent carbon partitioning between martensite and any retained austenite is usually not considered, because the temperature is too low for substantial amounts of diffusion to occur after quenching, and also because carbon supersaturation is usually eliminated by competing processes, e.g. carbide precipitation during tempering. There is, however, evidence that carbon partitioning from martensite

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to (retained) austenite does occur, to thin interlath films during cooling [3] or by isothermal holding in a Si-containing steel after transformation [4]. Carbide-free bainite microstructures may also form by diffusionless martensitic growth, followed by, or along with, carbon partitioning into austenite [1]. (It should be noted that the bainite transformation is not universally accepted to involve a shear mechanism, and also that it has been suggested that the term “bainite” should not be applied to carbide-free microstructures [5]). Carbon partitioning is one means of stabilizing austenite against further transformation at lower temperatures, and is likely to be especially important in these steels containing alloying additions (e.g. silicon) that suppress formation of iron carbides.

Carbon migration after martensite transformation is most often considered in the context of carbide precipitation reactions during tempering. Consequently, the thermodynamics of carbon partitioning between martensite and retained austenite have not been examined completely. Thus, the present work is focused on developing a model to address carbon partitioning from as-quenched martensite into austenite, under conditions where competing reactions are suppressed. (Such reactions include cementite or transition carbide formation, and decomposition of retained austenite by other processes such as bainite transformation.) The model does not address partitioning kinetics, but rather predicts the “endpoint” where partitioning is complete at a given partitioning temperature. The starting microstructure (i.e. initial fractions of martensite and retained austenite) is an input to the carbon partitioning model developed below, and may be controlled, for example, by the martensite transformation behavior (particularly the M_s temperature of the austenite in relation to the quenching temperature during heat treatment).

2. Thermodynamics of carbon partitioning

Under equilibrium conditions, mixtures of quenched martensite plus retained austenite in binary Fe-C alloys are expected to decompose to ferrite and iron carbide [6]. The phase compositions at equilibrium are given by the phase

boundaries on the usual Fe-C phase diagram, and the phase fractions may be determined from the lever rule. In the presence of substitutional (“X”) alloying additions, such as in a ternary Fe-C-X system, long-range diffusional processes at low temperature are limited primarily to carbon atom movements, and a “paraequilibrium” condition (following Hultgren [7,8]) is used to describe conditions where substitutional atoms do not partition between the phases during transformation, and thus the Fe/X atom ratios are unchanged in the different phases. It should be recognized that the usual paraequilibrium condition does not have meaning in the absence of substitutional alloying additions, i.e. in the Fe-C binary system. Thermodynamically, the paraequilibrium condition represents a minimum free energy condition, with the additional constraint that the Fe/X atom ratios are unchanged. A paraequilibrium transformation, such as proeutectoid ferrite precipitation from austenite at high undercooling, may proceed by interface migration involving short-range diffusion of the iron and substitutional atoms to accomplish the necessary structure change, along with long-range carbon diffusion to accomplish the necessary composition change. At paraequilibrium, the phase fractions and phase compositions are uniquely fixed, representing the minimum free energy condition in the absence of substitutional partitioning.

Under conditions where iron carbide precipitation is suppressed, then the phase diagram is of little use in predicting the metastable equilibrium condition that applies to heating of mixtures of martensite and retained austenite at temperatures well below the eutectoid temperature. The metastable equilibrium condition between martensite (i.e. ferrite) and austenite, identified by Hultgren [7,8], must therefore be considered. In the case of an Fe-C binary alloy, if the minimum free energy condition (“ortho-equilibrium”) applies, then the α and γ phase fractions and compositions would adjust themselves until the metastable α/γ ortho-equilibrium was achieved, where the chemical potentials (or partial molar free energies) of each component (Fe and C) would be equal in both the ferrite and austenite. In the presence of slow-diffusing substitutionals, the free energy minimization would be modified to represent a paraequilib-

rium condition in which the Fe/X ratios are fixed and the carbon potentials are equal in the phases. In either case, it is critical to recognize that the approach to metastability (i.e. to the appropriate minimum free energy condition) necessarily involves interface migration to adjust the phase fractions appropriately. When the position of the martensite/austenite interface is effectively fixed, as we consider here when examining carbon partitioning after martensite transformation is complete, then clearly it is *not possible* for the ferrite/austenite mixture to reach either orthoequilibrium (in Fe-C) or paraequilibrium (in Fe-C-X), and a new model is required.

The metastable condition representing the completion of carbon partitioning between martensite and austenite is developed below, and will be referred to as “constrained paraequilibrium,” or CPE. The constrained paraequilibrium condition is thus defined by *complete* absence of iron or substitutional atom movements, along with freedom of the carbon (or interstitial) atoms to migrate as needed. Like paraequilibrium, constrained paraequilibrium presumes that only carbon atoms move over distances greater than the unit cell dimensions. Unlike paraequilibrium, under constrained paraequilibrium conditions *short-range* movements of the iron and substitutionals do not occur at the interface and interface migration is thus precluded, hence the “constraint”. Constrained paraequilibrium also differs from paraequilibrium in that it applies to binary Fe-C alloys as well as higher-order systems containing substitutional alloying additions.

Constrained paraequilibrium can be readily understood through consideration of two key conditions that define its unique thermodynamic and matter balance constraints. First, carbon diffusion is completed under constrained paraequilibrium conditions when the chemical potential of carbon is equal in the ferrite and austenite phases, or equivalently, when the carbon activity is equal in the two phases (with reference to a common standard state). A similar condition has been invoked previously by Hillert and coworkers to describe a possible local boundary condition at the α/γ interface during bainite formation by a coupled diffusional/displacive process [9]. This thermodyn-

amic condition also represents a minimum free energy condition for the constrained system, but differs from (unconstrained) orthoequilibrium, which also requires that the chemical potential of iron must be equal in both phases. Second, the number of iron atoms must be conserved in each phase during the approach to constrained paraequilibrium. Such a matter balance is consistent with the presumption of a stationary α/γ interface after completion of martensite growth. While alloying elements such as silicon are important in promoting conditions where constrained paraequilibrium applies (i.e. where carbide formation is suppressed during tempering), the fundamentals of the constrained paraequilibrium condition apply equally well to the Fe-C binary system, which is used in the following discussion to derive and illustrate the properties of constrained paraequilibrium.

A schematic Gibbs molar free energy vs. composition diagram is shown in Fig. 1 for ferrite and austenite in the iron-carbon system at a given temperature. The chemical potential of a component in a phase ($\mu_{\text{component}}^{\text{phase}}$) is given by the tangent intercept with the respective composition axis. The common tangent construction in Fig. 1 thus illustrates the unique orthoequilibrium condition between ferrite and austenite at this temperature, showing the equilibrium phase compositions, X_{EQ}^{α} and X_{EQ}^{γ} . The same schematic free energy vs. composition curves for ferrite and austenite are reproduced in Fig. 2, along with two arbitrarily selected examples (I and II) satisfying the thermo-

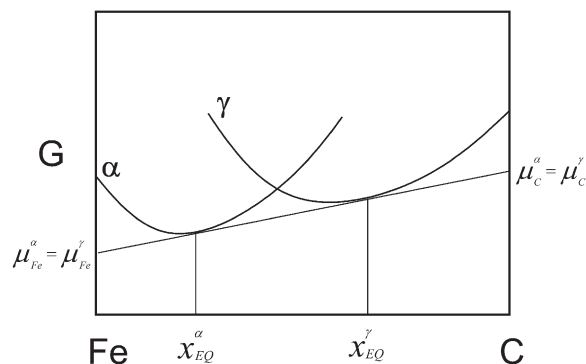


Fig. 1. Schematic Gibbs free energy vs. composition diagram showing the common-tangent construction representing orthoequilibrium between ferrite and austenite.

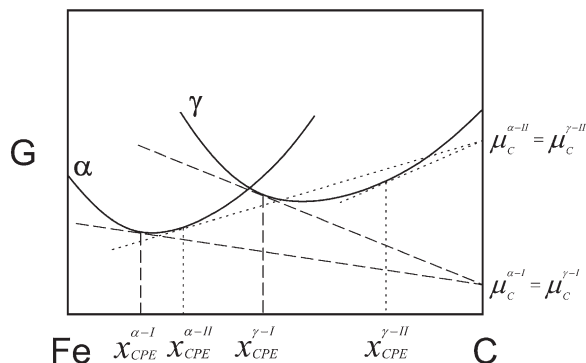


Fig. 2. Schematic Gibbs free energy vs. composition diagram showing two possible ferrite and austenite compositions satisfying the CPE requirement that the chemical potential of carbon is equal in the two phases.

dynamic condition for constrained paraequilibrium at this temperature. In each example, the tangents to the ferrite and austenite free energy curves intersect the carbon axis at a single point, indicating equal carbon potentials in α and γ , but the chemical potential of iron is clearly different in each phase, indicating that orthoequilibrium is not satisfied. (The orthoequilibrium condition *does* represent a possible constrained paraequilibrium condition, however.) This figure shows that there is not a unique ferrite and austenite composition that satisfies the general thermodynamic condition for constrained paraequilibrium at this temperature, but rather there is an *infinite set* of possible ferrite and austenite phase compositions. This is an important property of constrained paraequilibrium, where the matter balance constraint is also needed to uniquely determine the applicable phase compositions.

3. The constrained paraequilibrium condition in Fe-C alloys

The constrained paraequilibrium condition can be calculated for Fe-C alloys using published thermodynamic data, and knowledge of the as-quenched microstructure. Carbon activities in ferrite and austenite have been determined by Lobo and Geiger [10,11], with reference to graphite as

the standard state. For the purposes here, it is convenient to use the data in the simplified form [12]:

$$RT \ln \frac{\Gamma_C^\alpha}{\Gamma_C^\gamma} = 76,789 - 43.8T - (169,105 - 120.4T)X_C^\gamma \quad (1)$$

where Γ_C^α and Γ_C^γ represent the Henrian activity coefficients for carbon in ferrite and austenite, T is absolute temperature, R is the universal gas constant, and X_C^γ is the austenite composition (mole fraction of carbon). Since the activity of carbon in each phase is given by the product of the activity coefficient and the mole fraction of carbon, the condition whereby carbon activity is equal in the phases is satisfied when:

$$X_C^\alpha = X_C^\gamma \cdot e^{\frac{76,789 - 43.8T - (169,105 - 120.4T)X_C^\gamma}{RT}} \quad (2)$$

where X_C^α and X_C^γ represent the mole fractions of carbon in ferrite and austenite. The relationship in Eq. (2) describes a locus of phase compositions at any temperature; an example is shown in Fig. 3 that illustrates the appropriate ferrite and austenite compositions at 400 °C. The ferrite and austenite compositions in Fig. 3 are quite similar to previous results [9] determined using a different source of

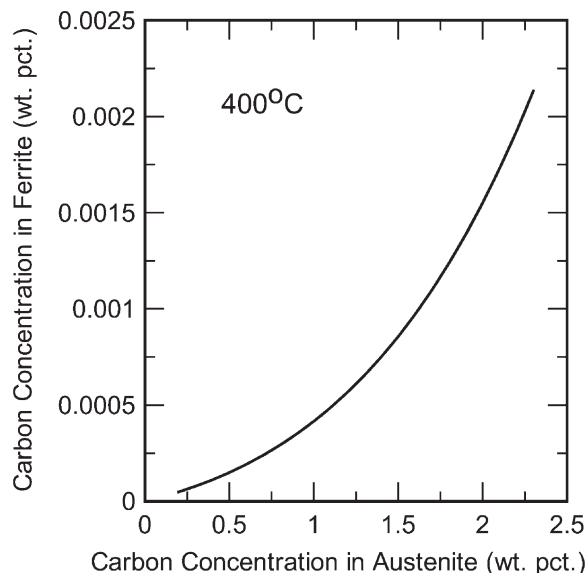


Fig. 3. Calculated locus of ferrite and austenite compositions having equal carbon activities at 400 °C.

free energy data [13]. In the CPE calculations presented below, temperatures between 200 and 600 °C are considered. The possible combinations of ferrite and austenite compositions over this range of temperatures are shown in Fig. 4. The results in Fig. 4 are indicative of reduced carbon solubility in ferrite at lower temperatures in this range.

Calculation of the constrained paraequilibrium condition for a particular steel requires two additional inputs to address the matter balance constraint: 1) the total carbon concentration, and 2) the fractions of martensite and retained austenite in the as-quenched condition. The phase fractions after martensite transformation are generally controlled by the degree of undercooling below the martensite-start (M_s) temperature of the austenite, according for example, to the Koistinen and Marburger equation [6]. The matter balance conditions account for changes in the phase compositions as carbon partitions between the phases, and the special CPE requirement that iron atoms are not transferred across the interface during partitioning, i.e. the number of iron atoms is conserved in each phase. For an initial condition (prior to any carbon

partitioning) where the martensite and austenite have identical compositions (i.e. the same as the overall carbon content of the steel, X_C^{alloy}) and the initial mole fractions of each phase are given by f_i^x and f_i^y , respectively, then the matter balance for iron is given by:

$$f_{CPE}^x(1 - X_{CPE}^y) = f_i^y(1 - X_C^{alloy}) \quad (3)$$

where f_{CPE}^x and X_{CPE}^y represent the austenite phase fraction and composition after partitioning, and we recognize that the iron concentration is always given by $X_{Fe}^y = 1 - X_C^y$ for binary alloys. It is perhaps counterintuitive that the phase fractions should change (i.e. $f_{CPE}^x \neq f_i^y$) under conditions where the α/γ interface is presumed to be constrained fully, but it should be clear that movement of carbon atoms between the phases necessarily involves a small adjustment in the total number of atoms in each phase, and thus the mole fractions of the phases. It also follows that the densities and lattice parameters of the phases may be changed slightly by carbon partitioning, which could lead to some elastic strain considerations that are not addressed here, and may be associated with some interesting effects that warrant investigation. The matter balance for carbon is straightforward, whereby the total carbon is given by the sum of the amounts in each of the phases, according to:

$$f_{CPE}^x X_{CPE}^x + f_{CPE}^y X_{CPE}^y = X_C^{alloy} \quad (4)$$

The constrained paraequilibrium condition is represented by the solution of four equations ((2), (3), (4) above, and (5) below), in four unknowns X_{CPE}^x , X_{CPE}^y , f_{CPE}^x , and f_{CPE}^y , where the relationship between the phase fractions is simply:

$$f_{CPE}^x + f_{CPE}^y = 1 \quad (5)$$

In this solution, the ferrite and austenite compositions in Eq. (2) take on their unique values, X_{CPE}^x and X_{CPE}^y , representing a specific constrained paraequilibrium condition.

The formulation illustrated here is strictly applicable to binary Fe-C alloys, but remains approximately correct for low alloy steels. Rigorous modification of the approach to account for alloying effects on the carbon activities would simply require adjustment of the activity coefficients in Eq. (1) using appropriate interaction parameters for

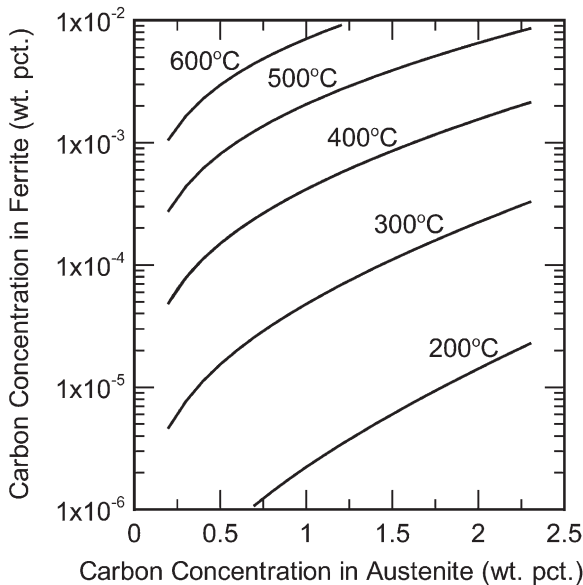


Fig. 4. Calculated loci of ferrite and austenite compositions having equal carbon activities at temperatures between 200 and 600 °C.

the elements of interest. Dislocation trapping could influence the distribution of carbon atoms [14], although effects on carbon solubility of the defect population in as-quenched martensite are not incorporated in the treatment here. A Zener ordering contribution to the carbon activity in ferrite is not required once partitioning has begun, and is thus not included here. Finally, the constrained paraequilibrium condition could potentially apply in some instances where the initial compositions of the ferrite and austenite phases are not identical, for example after completion of bainitic ferrite growth in carbide-free bainite microstructures. A more general expression for the iron matter balance then becomes:

$$f_{CPE}^{\gamma}(1 - X_{CPE}^{\gamma}) = f_i^{\gamma}(1 - X_i^{\gamma}) \quad (6)$$

where X_i^{γ} represents the carbon concentration in the austenite, prior to final carbon partitioning in the presence of a fully constrained interface.

4. Example calculations of constrained paraequilibrium

Determination of the CPE condition using the formulation presented in Eqs. (2)–(5) requires only the steel composition (i.e. carbon content), and the initial microstructure (mole fractions of martensite and retained austenite) to be specified. For example, we can consider an iron-carbon alloy containing 0.5 wt. pct. carbon, quenched to an initial condition where 75% (molar basis) martensite is present, along with 25% retained austenite. At a partitioning temperature of 400 °C, the calculations yield a solution for the CPE condition represented by:

$$W_{CPE}^{\alpha} = 0.0015\%, \quad W_{CPE}^{\gamma} = 1.97\%,$$

$$f_{CPE}^{\alpha} = 0.267, \quad \text{and} \quad f_{CPE}^{\gamma} = 0.733$$

where the CPE phase compositions in this instance (W_{CPE}^{α} and W_{CPE}^{γ}) are reported in wt. pct. The results illustrate substantial carbon partitioning between the phases, along with slight adjustment in the phase fractions due to carbon partitioning.

The constrained paraequilibrium phase compositions were calculated for a variety of Fe-C alloy

compositions having different mole fractions of martensite (or correspondingly, retained austenite) prior to a hypothetical CPE partitioning treatment. As mentioned previously, such differences in martensite fraction would be expected to arise from quenching to different temperatures below M_s , for example. Figs. 5, 6 and 7 present the calculated CPE phase compositions at temperatures between 200 and 600 °C for steels containing 0.25, 0.5, and 1.0% carbon by weight, respectively. Initial martensite (mole) fractions of 25, 50, 75, and 90% are shown to illustrate the results. Suppression of cementite formation becomes increasingly difficult at elevated temperature, [4] and thus temperatures above 600 °C were not considered. Furthermore, at elevated temperatures, the mobility of iron and substitutionals is eventually expected to become sufficient to allow short-range lattice reconstructive diffusion, at which time the fundamental basis of constrained paraequilibrium is violated, and a traditional paraequilibrium model (or orthoequilibrium in binary alloys) would be more applicable.

The results in Figs. 5–7 are of practical use for estimating the endpoint of carbon partitioning, but are also useful in illustrating important characteristics of constrained paraequilibrium. It is noteworthy that the CPE phase compositions are influenced by the alloy composition and the initial phase fractions, in addition to the temperature. In contrast, orthoequilibrium in the Fe-C binary system is represented by a *single* tie line at any temperature, with the phase compositions *independent* of the alloy composition. (Also, the phase fractions at orthoequilibrium adjust themselves to satisfy the lever rule for the appropriate alloy composition and phase compositions given by the tie-line, whereas the CPE phase fractions are only slightly changed during partitioning to account for carbon atom transfer across the constrained interface.) The results show that the CPE carbon concentration in ferrite increases with increasing temperature for a given initial condition, whereas the CPE carbon concentration in austenite decreases slightly with increasing temperature. The relative temperature dependence of the austenite composition is smaller, because the ferrite has a greater composition dependence of the carbon activity and quite low calculated solute carbon levels, and the austenite

0.25% Carbon

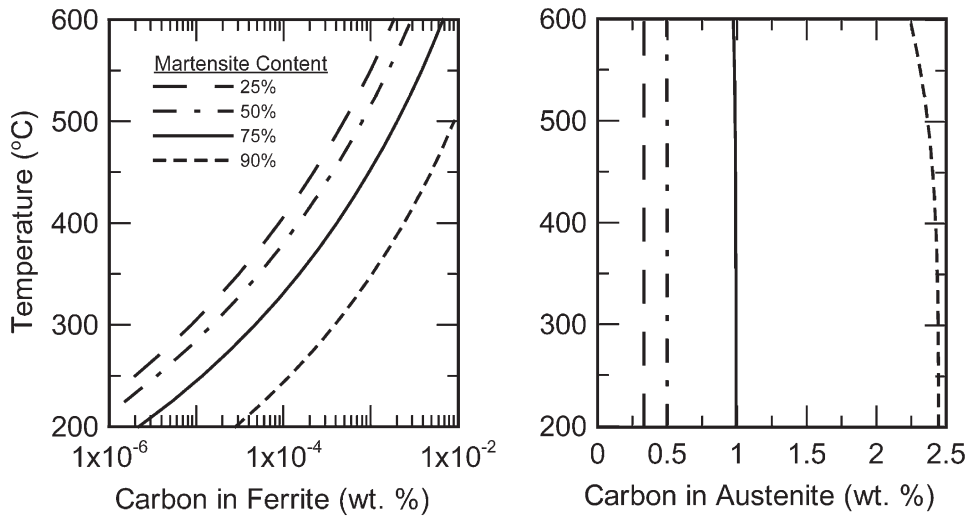


Fig. 5. Constrained paraequilibrium calculations for an Fe-0.25C (wt. pct.) alloy, showing the dependence of CPE ferrite and austenite compositions on temperature and initial martensite fraction (molar basis).

0.5% Carbon

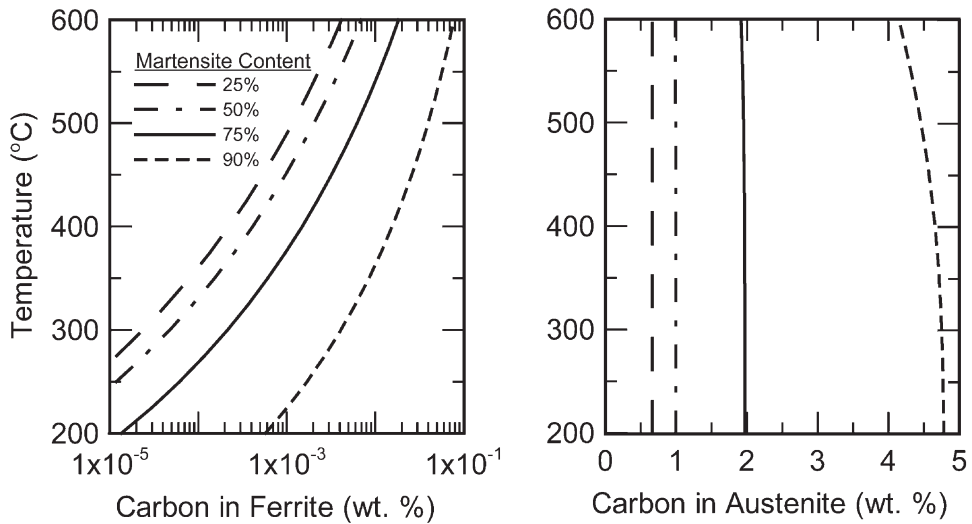


Fig. 6. Constrained paraequilibrium calculations for an Fe-0.5C (wt. pct.) alloy, showing the dependence of CPE ferrite and austenite compositions on temperature and initial martensite fraction (molar basis).

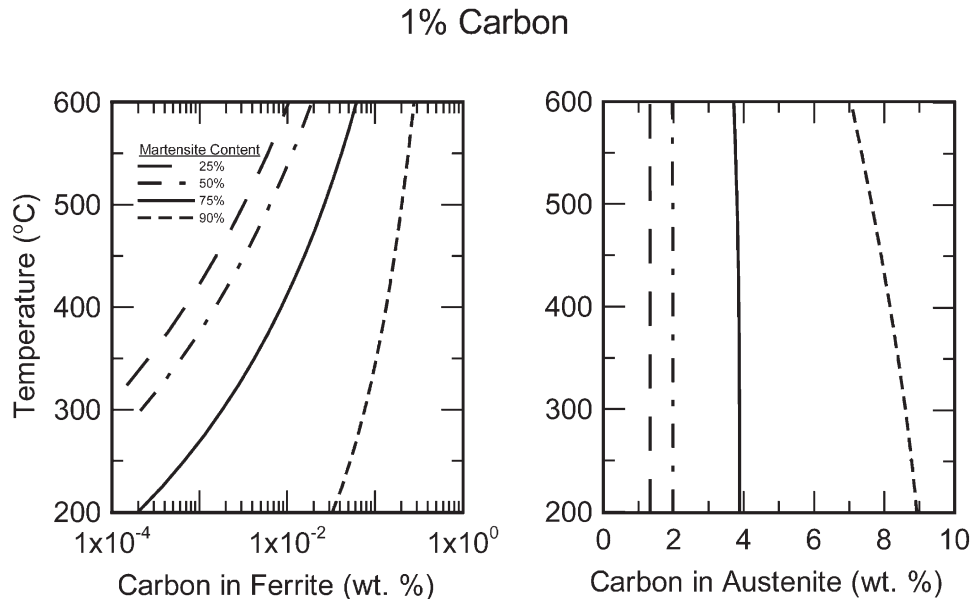


Fig. 7. Constrained paraequilibrium calculations for an Fe-1.0C (wt. pct.) alloy, showing the dependence of CPE ferrite and austenite compositions on temperature and initial martensite fraction (molar basis).

inherits most of the carbon in the steel at constrained paraequilibrium. The CPE condition is associated with phase compositions that can be either carbon-rich, or carbon-depleted, relative to orthoequilibrium. When the austenite fraction is greater than would be associated with orthoequilibrium, then the CPE phase compositions have carbon levels less than their orthoequilibrium values; and at austenite fractions less than the orthoequilibrium values, the CPE phase fractions have higher carbon levels. For a given initial martensite fraction, higher carbon steels have CPE phase compositions with greater carbon levels. Interestingly, the carbon levels in the retained austenite after CPE partitioning can be quite high, exceeding 2% even in the lowest carbon steel considered here (0.25% carbon), at a retained austenite fraction of 10%. Some caution is perhaps warranted when considering high predicted levels of carbon enrichment in the austenite. First, it should be recognized that the carbon activity data used for the calculations were determined in austenite compositions well below 1% carbon, and so extrapolation to much higher carbon levels should be only approximate. Second, the highest CPE austenite compositions calculated

here (for a 1% carbon steel containing 10% retained austenite) are greater than 6.7 wt. pct., and therefore exceed the carbon concentration of cementite! Consequently, it is implausible, or difficult, to envision conditions under which competing reactions such as carbide formation could be suppressed sufficiently to achieve constrained paraequilibrium in such instances. It is useful to recognize that an opportunity apparently exists to explore even greater silicon/aluminum levels than are typical of carbide-free bainitic steels, or to develop alternative alloying approaches to further suppress carbide precipitation, thereby enhancing the potential for employing new microstructures containing highly enriched austenite. Nonetheless, the overall conclusion of this model is clear: significant carbon enrichment of retained austenite should be possible by deliberate control of partitioning after martensite transformation.

5. Application of CPE partitioning

It is important to consider applications of CPE carbon partitioning and implications of the model

results, although some further alloy and process design considerations are also reported elsewhere [15]. It is envisioned that CPE partitioning will be most applicable for processing conditions where austenite is formed at elevated temperature (either during full austenitization or intercritical heat treatment), followed by cooling to a temperature carefully selected to control the fractions of martensite and retained austenite, and finally by a thermal treatment that accomplishes the desired extent of carbon partitioning. We refer to this processing sequence as Q&P (quenching and partitioning), to distinguish it mechanistically from conventional quenching and tempering (Q&T) of martensite, where carbide precipitation and decomposition of retained austenite are typical, rather than chemical stabilization of austenite by carbon partitioning.

Steels of greatest interest for Q&P processing will make use of controlled amounts of retained austenite, and include TRIP (transformation induced plasticity) sheet steels and high-strength carbide-free bainitic grades [16,17]. Alloying additions such as Si, Al or P are already present in these steels to suppress carbide formation [4], so major changes in alloy composition are not initially needed to apply the new process. The Q&P process can also be considered as a possible replacement for bainitic treatment in austempered ductile iron. In each example, carbon enrichment after martensite transformation is considered to replace bainite formation (where carbon partitioning to austenite is intimately coupled with ferrite growth). Decoupling of carbon partitioning and microstructure development (i.e. control of phase fractions and morphologies through athermal martensite transformation) represents a *dramatic and fundamental departure* from conventional approaches to microstructure control. There are widespread implications of this difference, including:

1. Greater amounts of carbon enrichment in austenite become possible when compared to conventional carbide-free bainites. It has been suggested that transformation to bainite by a shear mechanism effectively ceases when the austenite composition is enriched to T_o , the composition where the free energies of ferrite and austenite are equal. In contrast, much higher carbon levels in austenite are possible when partitioning occurs under CPE conditions reported above, given suitable control of the phase fractions after quenching. The CPE model also indicates that the phase compositions after partitioning in a given steel are identical in martensite/austenite mixtures compared to bainite/austenite mixtures, if the fraction of martensite is equal to the fraction of bainitic ferrite.
2. The temperature dependence of carbon enrichment is different for bainitic and Q&P processing. For bainite, the extent of partitioning is controlled by the temperature dependence of T_o , rather than the CPE conditions developed above.
3. The processes used to develop the phase fractions and morphologies in the final microstructure are completely separate from the carbon partitioning treatment, allowing complete and independent control during Q&P, whereas bainitic ferrite growth and carbon partitioning are effectively linked in the production of conventional carbide-free bainites. Different quenched microstructures can also be designed prior to partitioning, such as lath or twinned martensite, providing additional opportunity to influence final properties in new ways. For example, substantial amounts of carbon-depleted lath martensite could be used in TRIP sheet steels to achieve higher strength levels. Somewhat elevated carbon levels in ferrite might also be achievable by carefully controlling CPE conditions, increasing the strength of the ferritic matrix.
4. Microstructure evolution occurs by an athermal mechanism in the Q&P process, whereas bainitic transformation kinetics are thermally activated. The thermal history needed to obtain conventional carbide-free bainitic microstructure is influenced by many factors that control the TTT or CCT kinetics, whereas the M_s and quench temperatures largely control transformation during Q&P [15]. During the subsequent partitioning treatment, only carbon diffusion is needed, rather than carbon diffusion plus ferrite nucleation or growth. Decoupling of these processes likely leads to a different time dependence of the carbon partitioning, and allows greater flexibility in the intermediate tempera-

ture process when compared to bainite. For example, alloying additions made to increase hardenability or suppress ferrite formation during initial cooling from the intercritical or austenitizing temperature may substantially influence bainitic transformation kinetics, while only slightly influencing the Q&P process through small effects on the M_s temperature. While not of primary importance, it must be recognized that hardenability is still relevant in Q&P processing, influencing the response of the austenite during cooling or quenching, and also the propensity for competing microstructure changes during carbon partitioning.

5. Carbon enrichment of austenite can be employed in steels with microstructures that are traditionally martensitic, rather than just bainitic. For example, higher carbon austenites typical of moderately alloyed bearing steels or carburized gear steels are quenched and only tempered lightly, such that high hardness is preserved and significant quantities of austenite may be retained. The austenite can provide beneficial properties such as pitting resistance in rolling contact fatigue [18], and thus alloying modifications with suitable partitioning treatment could be used to alter the austenite stability, and thus the behavior in service. Similarly, in other alloys where substantial levels of silicon are currently applicable, such as ductile cast irons or martensitic steels (e.g. for tempering resistance in spring steels), Q&P treatments to influence the amount and character of the retained austenite may also be considered.

Finally, it is worthwhile to consider possible implications of the CPE partitioning model with respect to bainite transformation via a coupled diffusional/displacive [9,19,20] mechanism. In this context, the CPE model developed here predicts the *endpoint* of carbon partitioning in the presence of constrained interface boundaries, rather than processes occurring during bainitic transformation (i.e. when the boundaries are still moving). It follows that the final bainitic ferrite/retained austenite mixture in a carbide-free bainite should achieve constrained paraequilibrium when carbon partitioning is taken to completion. In such microstructures,

the final austenite composition has been reported by different studies [1,21] to approximate T_0 , and therefore to provide support for the displacive growth mechanism. The carbon concentration of bainitic ferrite is on the order of 0.03 wt. pct. [22] or greater [23], and is believed to be influenced significantly by trapping of solute carbon atoms by dislocations in the ferrite [24]. Most importantly, the steel is either *at* constrained paraequilibrium at the end of the bainite transformation, or else additional carbon partitioning must occur to achieve constrained paraequilibrium. While possible [23], such partitioning after completion of the bainite transformation is not emphasized in the literature, and indeed the remaining carbon available for partitioning from ferrite is rather small. Thus, it seems reasonable to conclude that the bainite transformation may be completed under near-CPE conditions, where the T_0 composition represents the CPE austenite composition.

The ferrite and austenite compositions at the interface *during* transformation are also of fundamental interest. Among the instantaneous interface compositions that have been considered for coupled diffusional/displacive growth of bainite are paraequilibrium [20] and “local equilibrium for carbon” [9]. Both the paraequilibrium and CPE condition are effectively subsets of this latter “local equilibrium” condition, which is effectively represented by any of the phase compositions satisfying Eq. (2) above. It is appealing to speculate that the interface compositions during growth of bainite could perhaps be given by the particular CPE phase compositions having the austenite composition of T_0 (where the appropriate free energies are adjusted for elastic strain energy, Zener ordering, and dislocation/solute interactions). That is, the transformation is not only *completed* under CPE conditions, but also may *proceed* under near-CPE conditions at the interface. Under such conditions, bainite growth might be considered to involve a diffusionless martensitic mechanism of interface migration, along with carbon diffusion-controlled growth kinetics with essentially *steady state* boundary conditions that are far from (para)equilibrium, and yet satisfy very reasonable thermodynamic constraints. In this theory, growth of a bainitic subunit is eventually inhibited both

by transformation strains and by the diminishing carbon concentration gradient in the austenite. The transition from bainitic to martensitic transformation is associated with the greater driving force and reduced carbon mobility at lower temperatures, both which allow growth to proceed quickly enough to avoid carbon buildup at the interface. While further work is needed to establish whether the kinetics and other characteristics of bainite formation are fully consistent with this explanation, the proposed behavior provides a model for the bainite transformation mechanism that is, at the same time, both “fully” diffusional and “fully” martensitic.

6. Conclusions

Consideration of carbon partitioning from quenched martensite to retained austenite in the presence of a stationary α/γ interface, under conditions where carbide precipitation is precluded, indicates that the metastable orthoequilibrium condition (or paraequilibrium in multicomponent alloys) between ferrite and austenite cannot be achieved. Consequently, a “constrained paraequilibrium” or CPE model was developed here to predict the endpoint of carbon partitioning in the presence of a stationary α/γ interface, i.e. applicable to the carbon redistribution processes after growth of the microstructural constituents is complete. It is shown that the CPE condition involves special matter balance constraints (such that the number of iron atoms is conserved in each phase during partitioning), while satisfying the thermodynamic condition where the chemical potential of carbon is equal in austenite and ferrite (i.e. carbon depleted martensite). Specific implications of the CPE model results include:

1. The ferrite and austenite compositions at constrained paraequilibrium are dependent on the steel composition and phase fractions, in addition to temperature, in contrast to orthoequilibrium in Fe-C alloys where the tie-line is dependent only on temperature.
2. The CPE carbon concentration in ferrite increases with increasing temperature for a

given initial condition, whereas the carbon concentration in austenite decreases with increasing temperature. The CPE phase compositions can be either carbon-rich, or carbon-depleted, relative to orthoequilibrium.

3. The austenite inherits most of the carbon in the steel at constrained paraequilibrium, and the retained austenite can be very enriched with carbon in some instances.
4. Applications of CPE partitioning may be considered in steels where carbide formation is suppressed (e.g. with Si, Al, P, or even Ni additions). The potential for a new “quenching and partitioning” process, or Q&P, is proposed, where the resulting martensite/austenite mixtures may be substituted for more conventional carbide-free bainitic microstructures such as high-strength TRIP sheet steels or even austempered ductile cast iron.
5. It is suggested that constrained paraequilibrium should also apply when partitioning is complete after transformation to carbide-free bainite microstructures. Austenite having a composition given by the T_0 curve is shown to represent a possible CPE condition, and it is speculated that bainite growth involving a martensitic mechanism of interface migration can occur with diffusion-controlled kinetics involving steady state boundary conditions corresponding to CPE compositions.

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