Balanced Constrained Carbon Equilibrium Accompanied by Carbide Precipitation

F.M. CASTRO CERDA, C. GOULAS, and L.A.I. KESTENS

The final carbon content of austenite in equilibrium with tempered martensite can be estimated by the so-called constrained carbon equilibrium in the presence of carbide (CCEθ) model. However, the linear predictions under CCEθ deviate from both the initial and the experimentally measured carbon content. A modified approach to the CCEθ model is proposed, which predicts an increase of the carbon content in austenite with the decrease of temperature below the onset of martensitic transformation.

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THE aim of quenching and partitioning (Q&P) of carbon steel is to produce a microstructure consisting primarily of martensite and stabilized austenite. The stabilization of austenite is achieved via carbon migration from martensite during the partitioning stage. This framework was probably the inspiration of Speer et *al.*[1] to propose an expression whereby the final carbon content of austenite (and the maximum fraction of stable austenite) is estimated under a constrained carbon equilibrium (termed CCE) condition between martensite and austenite. The CCE model is, thus, expressed under the conditions

$$\mu_C^{\alpha'} = \mu_C^{\gamma} \quad [1]$$

$$\mu_{Fe}^{\alpha'} \neq \mu_{Fe}^{\gamma} \quad [2]$$

$$X_C^{\alpha'} \times f_V^{\alpha'} + X_C^{\gamma} \times f_V^{\gamma} = X_C^0 \quad [3]$$

where μ_i^k is the chemical potential of i in the phase k, X_i^k is the mole fraction of i in the phase k, and f_V^k is the volume fraction of the phase k. X_C^0 represents the initial composition of the system in mole fraction. Metallographic observation of typical microstructures of low carbon steel subjected to Q&P will readily indicate that a suitable thermodynamic description of the system should consider the equilibrium between martensite, austenite, and carbide (see, for example[2–4]). Toji et *al.*[3] proposed a modification of the original CCE model by Speer et al.[1] considering the equilibrium of austenite with tempered martensite, the so-called CCEθ model. The degree of carbon enrichment of austenite is, thus, calculated in the latter after the precipitation of carbides in martensite (suggested to occur under paraequilibrium, PE, conditions). The CCEθ model is defined under the main constraint

$$\mu_C^{\alpha'} = \mu_C^{\theta} = \mu_C^{\gamma} \quad [4]$$

Notice that the model by Toji et al. does not take into account the mass balance of carbon. Adding the condition that carbon must be balanced between the three phases, i.e.,

$$X_C^{\alpha'} \times f_V^{\alpha'} + X_C^{\gamma} \times f_V^{\gamma} + X_C^{\theta} \times f_V^{\theta} = X_C^0 \quad [5]$$

one can estimate the equilibrium in a mixture of tempered martensite and austenite based on key features of both previous models, namely, (i) the equilibrium of α', θ, and γ and (ii) the mass balance. This new approach shall be called BCEθ thereon. In computing the carbon content of austenite (X_C^{γ}) under CCE, it is promptly realized that the carbon content increases as the temperature decreases below the M_S. Combining Eqs. [4] and [5] in[1] and solving for X_C^{γ} gives

$$X_C^{\gamma} = (X_C^0 - X_C^{\alpha'} \times f_V^{\alpha'}) \times \left(1 - f_V^{\alpha'}\right)^{-1} \quad [6]$$

$X_C^{\alpha'}$ estimated under PE between BCC and FCC phases is usually very small, and $f_V^{\alpha'}$ grows

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exponentially[5] as T decreases. Hence the expression is reduced to a constant divided by a factor which approaches to zero as the temperature decreases. A similar expression for X_C^{γ} is obtained from BCEθ model (Eq. [5]), whence

$$X_C^{\gamma} = (X_C^0 - X_C^{\alpha'} \times f_V^{\alpha'} - X_C^{\theta} \times f_V^{\theta}) \times (1 - f_V^{\alpha'} - f_V^{\theta})^{-1} \quad [7]$$

For $X_C^{\alpha'} \approx 0$, $X_C^{\theta'}$ is virtually constant and f_V^{θ} grows relatively slowly with decreasing temperature. Eq. [7] predicts a rather slower increment in X_C^{γ}, compared with CCE as the temperature decreases, by virtue of the factor $X_C^{\theta} \cdot f_V^{\theta}$. Comparison of Eqs. [6] and [7] indicates that (i) X_C^{γ} increases as the temperature decreases in both models and (ii) $X_{C,CCE}^{\gamma} > X_{C,\mathrm{BCE}\theta}^{\gamma}$ for $T < M_S$.

The solid black lines in Figure 1 show the calculation of CCE and BCEθ for a system of composition similar to that reported by Toji et *al.*[3] (1.07C-2.9Mn-2.2Si in wt. percent of C). The inferences (i) and (ii) made on the previous paragraph are consistent with the calculations shown in Figure 1. Calculations were run using ThermoCalc software, version 2020a, database TCFE9. X_C^{γ} under BCEθ was estimated for a α'/θ paraequilibrium when only C was the diffusing element (outlined circles in Figure 1), and when both C and Si (cross-circles in Figure 1) were allowed to partition. Despite that Toji *et al.*[3] do not elaborate on why their prediction yields $X_{C,CCE}^{\gamma} < X_{C,CCE\theta}^{\gamma}$ for temperatures slightly below M_S, (or for low fractions of martensite, as in their plot); it should be noticed that their model predicts a hypothetical transition from $\alpha' + \gamma$ equilibrium at low martensitic contents (slightly below the M_S) to $\alpha' + \gamma + \theta$ equilibrium. Notice also that both CCEθ calculi in [3] in fact predict a largely overestimated X_C^0 value at low temperatures (dashed blue curves in Figure 1). They argued that the CCEθ prediction should give a constant X_C^{γ} with temperature, based on the construction of the Gibbs free energy curves for the equilibrium between martensite, cementite, and austenite. The constant X_C^{γ} reported by Toji *et al.*[3] arises from the argument that the chemical potential of carbon in both martensite and austenite is equal during partitioning; thus, a change in the fraction of martensite with temperature should not influence X_C^{γ}. This is actually true whenever the system is allowed to adjust the phase fractions according to the mass balance, i.e., $f_V^{\alpha'}$, f_V^{γ}, and f_V^{θ}. In the case of Q&P, it is considered that the phase fractions are fixed; thus, the degrees of freedom left to the system to attain equilibrium are $X_C^{\alpha'}$ and X_C^{γ}, (X_C^{θ} is constant). Consequently, the final carbon content in austenite (the predicted $X_{C,CCE\theta}^{\gamma}$) should not be solely estimated from the condition $\mu_C^{\alpha'} = \mu_C^{\gamma}$. To illustrate this, Figure 2 (black solid line) shows the temperature variation of μ_C for a system similar to that studied by Toji *et al.*[3] The carbon content of austenite under PE with tempered martensite, as estimated from μ_C, is shown as a dashed blue line in Figure 2. Finally, the initial carbon content calculated from the mass balance ($X_C^0\_\mu_C$ in Eq. [2]) correspond to the solid blue line in Figure 2. The overestimation of C content which arises from determining X_C^{γ} under CCEθ from the condition $\mu_C^{\alpha'} = \mu_C^{\gamma}$ becomes evident when comparing the actual initial composition (red dashed line in Figure 2), with the recalculated average carbon content values under the same condition. Else, $\mu_C^{\alpha'} = \mu_C^{\gamma}$ yields values of X_C^{γ} unrealistically high (cf. solid blue line

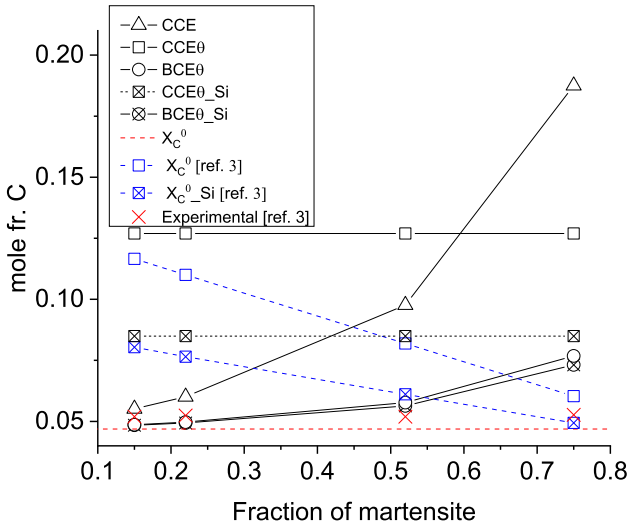

Fig. 1—CCE, CCEθ, and BCEθ calculations of carbon content in austenite (X_C^{γ}), using the system and experimental phase fractions below the M_S reported by Toji *et al.*[3] Black solid lines represent CCE, CCEθ, and BCEθ conditions (triangles, squares and circles, respectively). Blue dashed lines are recalculations of the initial carbon content of the system, as predicted by the reported $X_{C,CCE\theta}{}^{\gamma}$ in Ref. [3] The red dashed line denotes the initial carbon content of the system. CCEθ_Si, BCEθ_Si, and X_C^0_Si were calculated under PE allowing the partition of Si between α' and θ. Red crosses mark experimental measurements of carbon content in austenite (Color figure online).

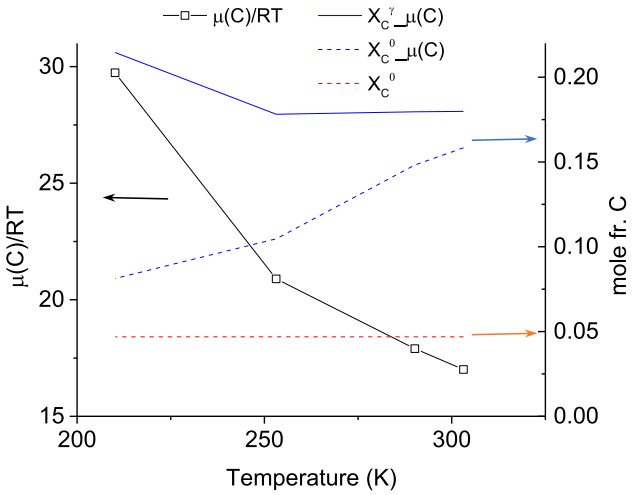

Fig. 2—Temperature variation of the paraequilibrium chemical potential of C (μ_C) in austenite in equilibrium with tempered martensite (solid black line, the ordinate at the left hand side). The carbon content of austenite ($X_C^{\gamma}\_\mu_C$, blue solid line) and initial carbon content ($X_C^0\_\mu_C$ blue dashed line) were recalculated from values of μ_C. The red dashed line denotes the initial carbon content of the system (Color figure online).

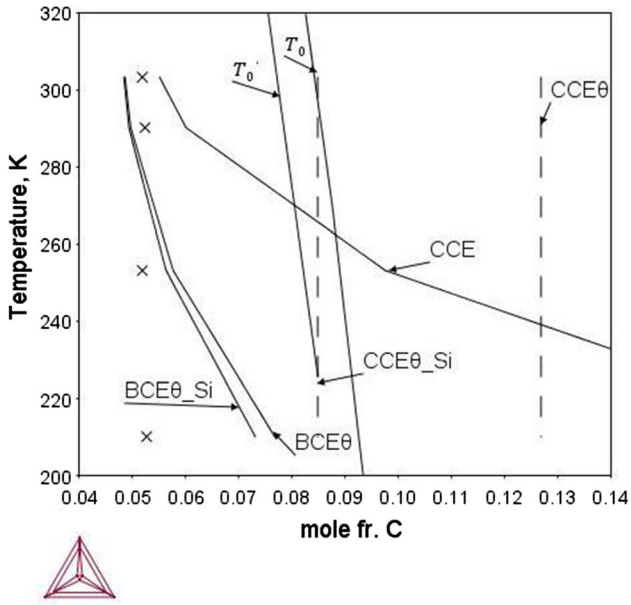

Fig. 3—Isopleth section of the phase diagram showing the calculations of X_C^{γ} according to both CCE and BCEθ models. Crosses denote experimental data by Toji *et al.*[3]

X_C^{γ}_ μ_C in Figure 2), even higher than that predicted via CCE model at low temperatures (low $f_V^{\alpha'}$). It should be pointed out that according to the calculations under the imposed $\mu_C^{\alpha'} = \mu_C^{\gamma}$ condition, X_C^{γ} seems to slightly decrease with temperature, which ought to be related to the retrograde nature of $X_C^{\gamma/\alpha}$ solvus line.[6]

Figure 3 shows the experimental data reported by Toji *et al.*[3] (crosses) compared with the predicted carbon content in austenite under CCE and BCEθ models, i.e., considering the mass balance. The data correspond to samples quenched at different temperatures and partitioned at the same temperature and time (673 K, 300 s). Figure 3 also includes the T_0 and T_0' curves. T_0 represents the compositions for equal Gibbs free energy of BCC and FCC phases, whereas T_0' is calculated with additional energy term to the BCC phase (400 Jmol^{-1}). It is observed that the fit to the BCEθ predictions is reasonable at temperatures close to the M_S, whereas the experimental data do not correspond well to the BCEθ prediction at temperatures well below the M_S. In the study by Toji *et al.*,[3] conversely, the experimental data fit better the CCE model for temperatures right below the M_S, but it is still far from their constant CCEθ prediction for lower temperatures. From the microstructural point of view, it is reasonable to expect a better fit of the experimental data to BCEθ (cf. Figure 3) because the phase distribution is much more accurately described in the BCEθ model than in the CCE model. However, the constant value of the experimental carbon content is still not understood. It has been suggested[7] that plate martensite has comparatively less defects than lath martensite; thus, carbon is forced to remain in the interstitial sites. The diffusion of C is consequently hindered and thus poor carbon redistribution, as the one experimentally reported by Toji *et al.*,[3] could be expected.

In summary, a modified model is proposed for the prediction of carbon content in austenite in Q&P treatment, which includes the mass balance of carbon into the $\alpha' + \gamma + \theta$ equilibrium. According to the new model, it is pointed out that at temperatures below the M_S (i) X_C^{γ} should increase as the temperature decreases, and (ii) $X_{C,CCE}^{\gamma} > X_{C,BCE\theta}^{\gamma}$.

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