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Communication

Numerical Investigations of the Effects of Substitutional Elements on the Interface Conditions During Partitioning in Quenching and Partitioning Steels

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In quenched and partitioned steels, carbon partitioning is considered to be driven by a constraint para-equilibrium at the martensite/austenite interface. Using Thermo-Calc calculations, we investigated the effect of non-partitioned elements on the resulting interface condition. Among all tested elements, only aluminum and chromium have significant effects. From this numerical study, a practical composition- and temperature-dependent relationship describing interface tie lines was derived and calibrated for Fe-C-2.5Mn-1.5-Si-X wt pct alloys (X = Cr or Al).

The quenching and partitioning (Q&P) process was invented by Speer *et al.*, to meet the needs of the automotive sector for the development of a third-generation advanced high-strength steel.^[1,2] Q&P steels show mainly duplex ultrafine microstructures made of martensite and residual austenite. These typical microstructures are obtained by (1) an initial quench after austenitization down to a temperature QT (quench temperature) between the martensite start (Ms) and finish (Mf) temperature of the alloy to induce a partial martensitic transformation, (2) an isothermal holding

treatment at the partitioning temperature (PT), identical to or higher than the QT to promote carbon diffusion out from martensite to stabilize austenite, and (3) a final quench from the partitioning temperature to room temperature.

During step (2), at PT, carbon partitioning from martensite to austenite is one of the key phenomena that occur during the Q&P process. Its kinetics is governed by carbon diffusion in martensite and austenite, respectively, and by the carbon concentrations on each side of the martensite/austenite interface. This boundary condition is often assumed to be governed by constrained para-equilibrium (CPE). This CPE imposes first no partition of substitutional elements (accounting for their supposed low diffusivity at PT), continuity of the carbon chemical potential across the interface, no interface mobility and, finally, absence of any carbide precipitation.^[1]

In this article, we focus only on the thermodynamic conditions at the interface to determine all the possible tie lines for a given temperature and alloy composition, *i.e.*, the relations between carbon concentrations at interfaces in both austenite and martensite. As shown by Speers,^[1] a carbon mass balance and the assumption of interface mobility permit calculating the final state after partitioning.

Few previous works have proposed practical laws derived from thermodynamic calculations describing these tie lines but solely in binary Fe-C steels, neglecting the effect of substitutional elements.^[1,3] Nevertheless, most alloys used to study or produce Q&P steels contain high amounts of alloying elements, such as manganese, which contributes to increasing the hardenability of the steel or the silicon, which helps retard cementite carbide precipitation.^[4] Aluminum can be added instead for a supposed similar effect on carbide precipitation as investigated in References 4 and 5 although 6 and 7 showed aluminum neutrality on cementite carbide precipitation.

In this work, the influence of classical alloying elements and temperature on the CPE condition was systematically investigated by thermodynamic calculations using Thermo-Calc[®] software. The calculations were first conducted taking the binary Fe-C system as a reference. We deduced from this work that only aluminum and chromium have a significant effect on the interface condition, and we established a composition- and temperature-dependent relationship for a typical Fe-2.5Mn-1.5Si-X wt pct alloy (X = Al or Cr).

In the calculations conducted below, we consider a martensite/austenite interface at temperature PT. The objective of the numerical procedure is to establish a relationship between carbon contents at the interface in martensite and austenite, respectively.

The thermodynamic conditions derived from CPE at temperature PT are defined by two equalities:

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

where $u_i = x_i/(1 - x_C)$, with x_i the atomic concentration of substitutional element i and x_C that of carbon. The u fraction of substitutional element i represents its amount in the substitutional lattice in martensite (α') or austenite (γ).

$$\mu_C^{\alpha'} = \mu_C^{\gamma} \quad [2]$$

where $\mu_C^{\alpha'}$ and μ_C^{γ} are the carbon chemical potentials in martensite (α') and austenite (γ), respectively.

This set of equations allows one degree of freedom. This allows establishing a relationship between $w_C^{\alpha'}$ and w_C^{γ} , *i.e.*, the weight carbon concentration in martensite (α') and austenite (γ), respectively.^[8] In this study, calculations were performed using the S version of Thermo-Calc[®] software. The CPE relationship was established in two steps. First, the relationship between μ_C^{ϕ} and w_C^{ϕ} ($\phi = \alpha'$ or γ) was established separately in each phase α' and γ . Second, both calculations were combined considering Eq. [2] to obtain the CPE relationship. This method permits describing all the possible tie lines at interfaces during partitioning. To determine the operative tie lines, it is necessary to carry out a thermokinetic calculation involving a carbon mass balance between phases. These last calculations are beyond the scope of this short communication solely dedicated to the thermodynamic aspects.

Three databases were used: SSOL4, TCFE7 and TCFE9. In these commercial databases, the martensite phase has not been described explicitly so far (even in the most recent ones). This is why we decided to use the ferrite phase to represent the behavior of martensite even if far higher carbon concentrations can be expected (up to 0.5 wt pct in martensite at 400 °C, for instance).^[9,10]

For the same calculations, the tested databases gave significantly different results. The carbon contents found in ferrite were also systematically lower than the relationship proposed for a Fe-C binary system^[3] by Santofimia *et al.* who used another source of thermodynamic data, MTDATA. One also has to mention that the thermodynamic data regarding the metastable α'/γ equilibrium came in large part from extrapolations far below the eutectoid temperature.^[11] Nevertheless, the trend for each database was identical, which is a reason why we decided in a first step to study only the relative effects of alloying elements using a single database keeping in mind that the absolute carbon concentrations found in the phases can always be discussed. We chose to use the TCFE7 database to offer a continuous and stable description of the CPE condition as the latest database (TCFE9) shows a discontinuity when varying the temperature.

Figure 1 shows the evolution of the weight carbon content in ferrite as a function of the weight carbon content in austenite under the CPE condition for different Fe-C-X systems where X is (a) manganese, (b) silicon, (c) aluminum, (d) chromium, (e) nickel and (f) molybdenum at 673 K. The black curve represents

the CPE interface conditions for the binary Fe-C system at the same temperature, *i.e.*, all the possible tie lines for this particular equilibrium. For each element, three different levels of alloying element addition were considered (1.5, 2.5 and 3.5 wt pct for manganese and 0.5, 1.5 and 2.5 wt pct respectively for the other elements).

Manganese, chromium and molybdenum increase the carbon content in ferrite for a given carbon content in austenite (the slope of the curve describing the CPE interface condition increases). The only significant increase was however observed for chromium.

On the contrary, aluminum, nickel and silicon decrease the carbon content in ferrite for a given carbon content in austenite (the slope of the curve describing the CPE interface condition decreases). The only significant decrease was however observed for aluminum.

In addition, the effects of phosphorus and cobalt additions were also investigated (with content ranging from 0 to 0.1 wt pct for phosphorus considered as a substitutional element^[12] and from 0 to 1 wt pct for cobalt). Both elements show a negligible effect on the CPE interface condition.

These trends have been observed at different temperatures, suggesting that among all the tested elements only aluminum and chromium additions significantly affect the interface conditions. We can expect that the addition of aluminum will increase the partitioning kinetics by increasing the carbon concentration in austenite and thus increasing the carbon gradients at the interface. Chromium is supposed to affect the partitioning mechanism in the opposite way.

To go farther, we numerically investigated the effect of aluminum and chromium addition on a reference quaternary alloy. We chose the alloy Fe-C-2.5Mn-1.5Si studied by our group^[13] without losing generality, as manganese and silicon have independently weak effects. We verified that the cross effects of alloying elements are limited. This reference alloy is also interesting as it is the basis of a few studies on Q&P steels.^[13-16]

The interface conditions were thus studied in Fe-C-2.5Mn-1.5Si-X wt pct (X = Al or Cr) alloys at different temperatures (between 373 K and 773 K with 50-K steps) and with X additions up to 4 wt pct with 0.5 wt pct steps. To capture the observed variations in CPE conditions due to both alloying elements, we calibrated a composition- and temperature-dependent relationship on raw Thermo-calc[®] results. Inspired by the prior work of Santofimia *et al.*, the following empirical equations were considered:

$$w_C^{\alpha'} = w_C^{\gamma} e^{(a_T + c_X) w_C^{\gamma} + (b_T + d_X)} \quad [3]$$

where a_T and b_T are temperature-dependent functions (T the temperature in K) and c_X and d_X are temperature- and composition-dependent functions for both elements (Al or Cr). w_C^i is the weight concentration of carbon in austenite and martensite. This formalism permits isolating the composition and temperature effects. Possible cross effects between alloying elements are once again neglected. In the absence of alloying elements ($w_X = 0$), Eq. [3] can be drastically simplified into Eq. [4], which can then be used to describe the CPE condition of the reference alloy.

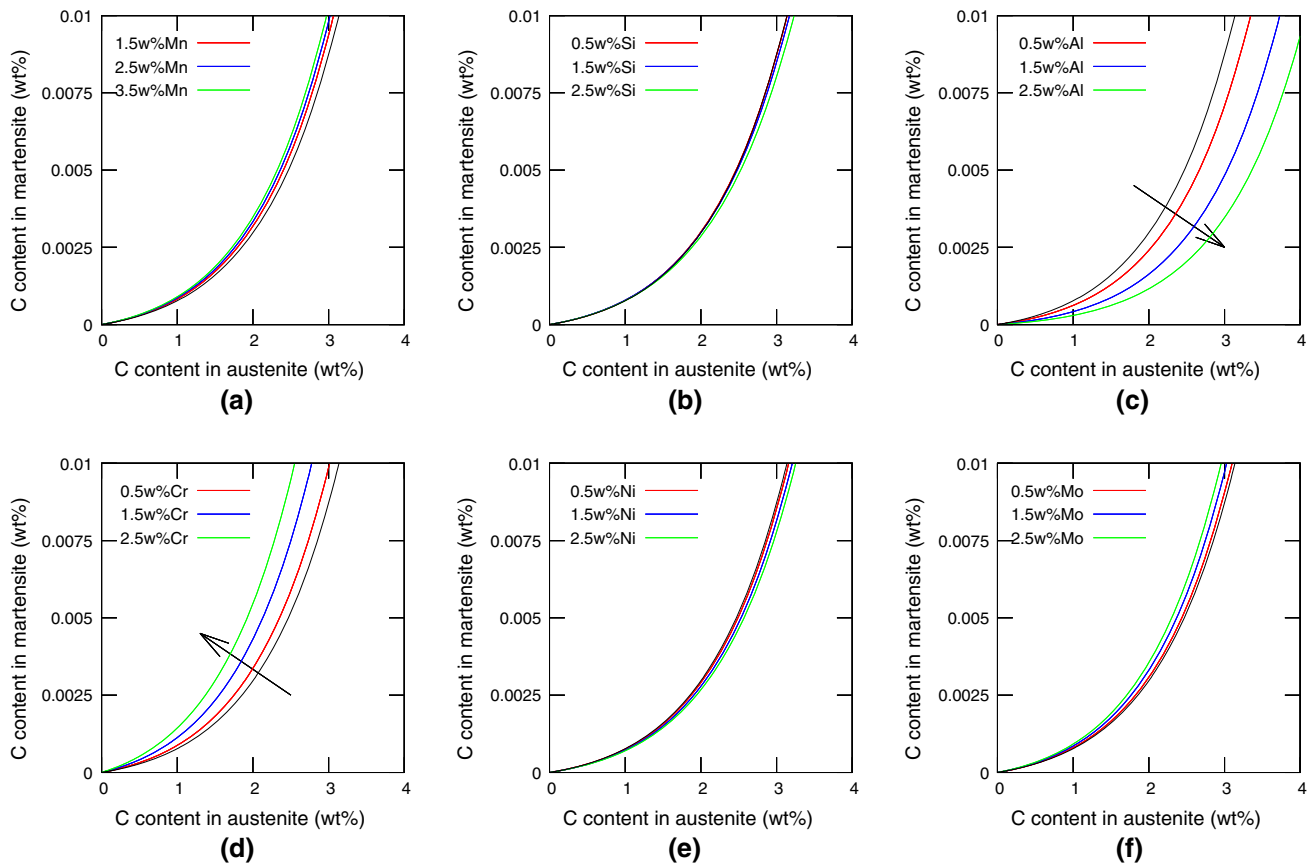


Fig. 1—Effect of substitutional alloying elements at 673 K on the CPE condition: (a) manganese, (b) silicon, (c) aluminum, (d) chromium, (e) nickel and (f) molybdenum. The black curve is the reference of the CPE condition for a binary Fe-C steel. The carbon content ranges in austenite and martensite correspond to the levels generally found in local field thermokinetic models in the literature.

Table I. Numerical Values of Parameters a_i and b_i as Defined in Eqs. [5] and [6] After Calibration

a_0	a_1	a_2	a_3
338.559	$-9.456 \cdot 10^{-1}$	$1.193 \cdot 10^{-3}$	$-5.664 \cdot 10^{-7}$
b_0	b_1	b_2	b_3
-56.107	$1.663 \cdot 10^{-1}$	$-2.016 \cdot 10^{-4}$	$9.033 \cdot 10^{-8}$

These parameters permit capturing the temperature sensitivity of the CPE condition for the reference alloy Fe-C-2.5Mn-1.5Si wt pct in the temperature range 373 K to 773 K generally chosen for PT.

$$w_c^{\alpha'} = w_c^{\gamma} e^{(a_T(T) w_c^{\gamma} + b_T(T))} \quad [4]$$

$$c_X(w_X, T) = c_0 w_X + c_1 w_X^2 + c_2 w_X T \quad [7]$$

a_T and b_T are described by third-order polynomials:

$$d_X(w_X, T) = d_0 w_X + d_1 w_X^2 + d_2 w_X T \quad [8]$$

$$a_T(T) = a_0 + a_1 T + a_2 T^2 + a_3 T^3 \quad [5]$$

$$b_T(T) = b_0 + b_1 T + b_2 T^2 + b_3 T^3 \quad [6]$$

c_X and d_X are functions of the temperature and alloying additions:

Parameters a_i and b_i must first be adjusted on the reference alloy. Parameters c_i and d_i are then adjusted for varying aluminum and chromium additions, respectively. In all the cases, the parameters were calibrated using a mean square method to minimize the deviation from the thermodynamic calculations and result of

Table II. Numerical Values of Parameters c_i and d_i as Defined in Eqs. [7] and [8] After Calibration to Capture the Effect of Aluminum and Chromium Additions

Al	c_0	c_1	c_2
	156.193	- 389.189	- 6.054 10^{-2}
Cr	d_0	d_1	d_2
	- 100.250	210.517	8.469 10^{-2}
Cr	c_0	c_1	c_2
	- 69.285	164.219	- 5.467 10^{-2}
Cr	d_0	d_1	d_2
	87.991	- 129.354	- 8.556 10^{-2}

In addition, with parameters a_i and b_i given in Table I, these parameters permit describing the CPE condition for Fe-C-2.5Mn-1.5Si-X wt pct alloys in the temperature range 373 K to 773 K.

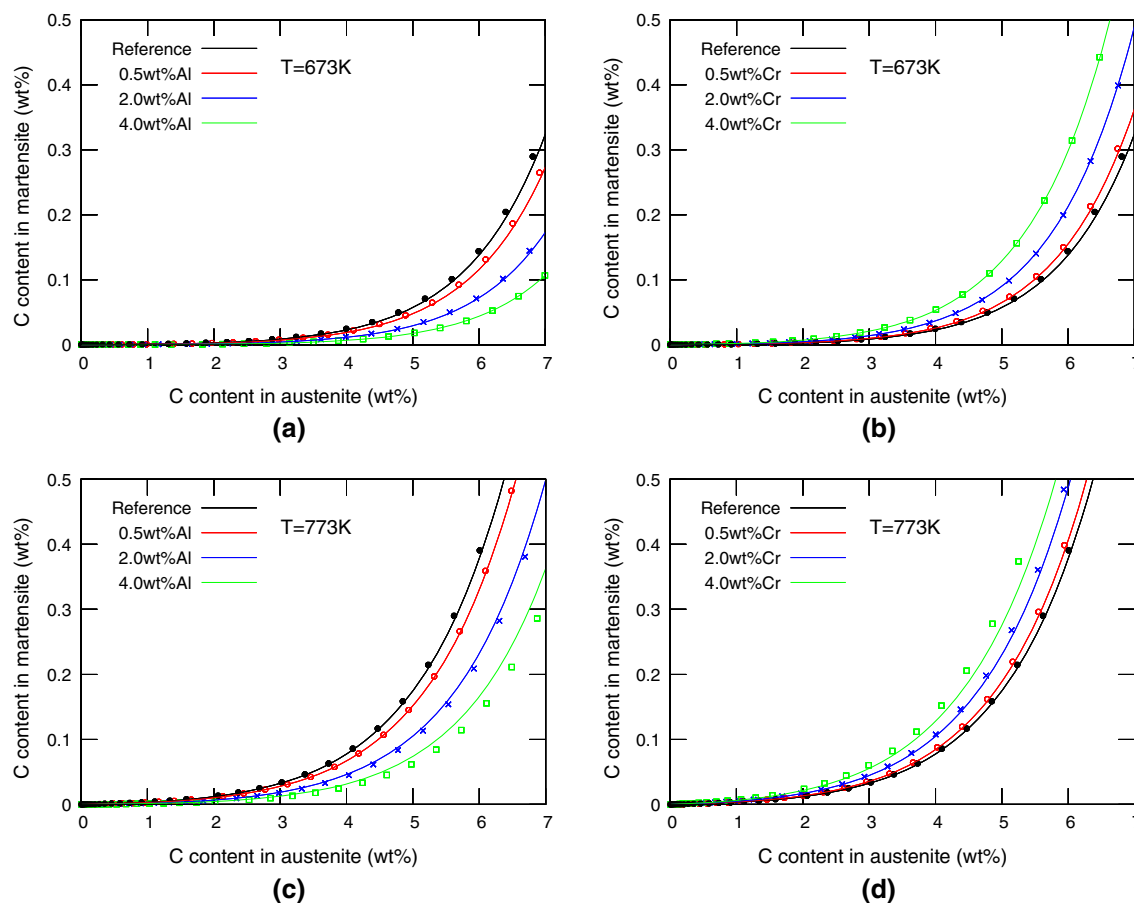


Fig. 2—Carbon composition at martensite/austenite interfaces predicted by a CPE interface condition for Fe-C-2.5Mn-1.5Si-X wt pct alloys (X = Al or Cr) at 673 and 773 K. (a) X = Al, T = 673 K; (b) X = Cr, T = 673 K; (c) X = Al, T = 773 K; (d) X = Cr, T = 773 K. The black curves represent the CPE condition for the reference alloy Fe-C-2.5Mn-1.5Si wt pct (Eq. [4]). The dots are the results of the thermodynamic computation performed with Thermo-Calc[®] software and the TCFE7 database, and the continuous lines are calculated with Eq. [3] after calibration.

Eq. [3]. The maximum relative error made using the proposed relationship is lower than 0.5 pct in the studied ranges of compositions and temperatures. The numerical values of the parameters calibrated on raw Thermo-Calc[®]'s results are given in Tables I and II.

Figure 2 represents the result of raw thermodynamic calculation (dots) and the result of Eq. [3] after calibration (continuous lines) corresponding to the CPE conditions of Fe-C-2.5Mn-1.5Si-X wt pct alloys

(X = Al or Cr) at 673 K and 773 K. Figures 2(a) and (c) corresponds to aluminum additions and Figures 2(b) and (d) to chromium additions. The correlation is excellent in all the cases.

Our relationship permits good reproduction of the temperature sensitivity of the CPE condition. Increasing PT leads in fact to a decrease in the carbon concentration in austenite^[1,3] and thus to slower partitioning kinetics. An addition of aluminum

increases the carbon concentration in austenite, contrary to chromium, as already shown in Figure 1. This qualitatively confirms that cross effects between alloying elements (Mn/Si with Al/Cr) are limited for such calculations.

To summarize, the influence of substitutional alloying elements on the CPE interface condition was thoroughly investigated based on calculations with Thermo-Calc[®] software with the TCFE7 database. This interface condition is often met at the martensite/austenite interface during the partitioning step of Q&P treatments.

Except aluminum and chromium, all the investigated elements (manganese, silicon, nickel, molybdenum, phosphorus and cobalt) have a weak effect on the carbon composition at the interface. On the contrary, aluminum addition increases the carbon content in the austenite and is expected to accelerate carbon redistribution between martensite and austenite. The opposite effect is expected with chromium addition.

Finally, a composition- and temperature-dependent relationship is proposed to describe these effects. The law was calibrated for a Fe-C-2.5Mn-1.5-Si-X wt pct alloy (X = Al or Cr limited to 4 wt pct) for temperatures between 373 K and 773 K with excellent agreement. This explicit relationship may prove to be practical when conducting local field calculations of carbon diffusion at martensite/austenite interfaces in Q&P steel as it permits avoiding time-consuming direct couplings with thermodynamic databases.

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