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Implication of elastic coherency in secondary hardening of high Co–Ni martensitic steels

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Composition and stoichiometry of coherent M_2C carbide precipitates, (M = Cr, Mo, Fe), in two high Co–Ni martensitic steels have been calculated using thermodynamic conditions for mechanical, chemical and interfacial equilibrium between the ferrite (tempered martensite) and the M_2C phase. Compared to the corresponding incoherent equilibrium compositions, our calculations at the standard secondary hardening temperature of 783 K predict a substantial carbon deficiency and a measurable solubility of iron in the M_2C phase, both of which have been verified experimentally. These deviations from the incoherent equilibrium compositions are found to be in line with the influence of these constituents in lowering the strain energy by reducing the principal strains of the M_2C stress-free transformation strain.

1. Introduction

Superior combination of strength and fracture toughness in secondary-hardened high Co–Ni martensitic steels is achieved through fine-scale precipitation of metastable M_2C carbides, (M = Cr, Mo, Fe), in a ductile Fe–Ni–Co ferrite (tempered martensite) matrix. First of these steels, the HP 9-4-X series, containing 9Ni, 4Co, 1Cr, 1Mo, 0.5V, and 0.20–0.45C (wt %) was developed by The Republic Steel Corporation in 1974 [1]. Following the work of Speich *et al.* [2] The United States Steel Technology soon followed with its HY180 alloy containing 10Ni, 8Co, 2Cr, 1Mo and 0.12C (wt %). In 1978 The General Dynamics introduced its AF1410 steel with 14Co, 10Ni, 2Cr, 1Mo and 0.16C (wt %), which combines high strength (UTS = 1600–1750 MPa, HRC = 50–55) with high fracture toughness ($K_{IC} > 130$ MPa m$^{1/2}$) [3]. Recently an experimental alloy SRG1 containing 16Co, 5Ni, 4Mo and 0.25C (wt %) was developed by the Steel Research Group at MIT [4], in order to carry out a fundamental study of the kinematics of M_2C precipitation during secondary hardening reaction.

The final heat treatment which imparts the optimum combination of strength and toughness in high Co–Ni martensitic steels is 5–8 h temper at 783 K. This treatment ensures nearly complete dissolution of a transient cementite phase (forms early in the course of tempering) before excessive dissolution of M_2C and the attendant formation of stable M_6C and $M_{23}C_6$ carbide phases could take place. The cementite dissolution by completion of alloy carbide precipitation is essential to toughness enhancement, as cementite particles promote microvoid nucleation and thus limit fracture toughness in this class of steels [4]. On the other hand, the stable carbides are also detrimental to the properties and typically give rise to a simultaneous degradation of both strength and toughness. Complete understanding of the phase sequence and the basic structure/property relationships in high Co–Ni steels, discussed above, entails knowledge of major phase equilibria such as ferrite/M_2C equilibrium.

Examination of secondary hardening behaviour in AF1410 steel at the standard tempering temperature of 783 K [5] shows that M_2C carbide particles "overage" after approximately 15 min. Particle size and lattice parameter measurements carried out recently by Montgomery and Olson [6], indicate that the M_2C phase loses coherency after 16 h at 783 K. Upon the standard 5–8 h heat treatment. M_2C particles are thus in an overaged condition yet fully coherent. It is well established that phase equilibria in coherent solids are significantly different than that in incoherent solids due to a strong coupling between the thermodynamic conditions necessary for chemical, mechanical and interfacial equilibrium [7, 8]. For example, only specific systems will allow the equilibrium conditions to be satisfied simultaneously. Two of such cases, in elastically isotropic systems where the strain relating unit cells of the two phases in the absence of stress, the stress-free transformation strain, is a composition independent pure dilation, have been identified by Cahn and Larche [7] and Johnson and Voorhees [8].

In the present paper we analyse the effect of elastic coherency on the nucleation of M_2C carbides and the ferrite/M_2C equilibrium, a system where the stress-free transformation strain is a general composition dependent orthorhombic strain and where the isotropic elastic constants differ in the two phases.

2. Procedure

To evaluate coherent phase equilibrium between the ferrite (α-phase) and the M_2C carbide (β-phase) we utilize conditions for mechanical, chemical and interfacial equilibrium. It is assumed that the precipitation phase has a uniform composition. Since the mole

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fraction of β in AF1410 and SRG1 steels is very small, less than 0.02, the interaction between β-particles can be ignored resulting in a constant stress field and hence a uniform composition in this phase. On the other hand, the stress field in α is not uniform and neither is the α-composition. When the structure of α remains cubic regardless of the composition, the α stress-free transformation strain $e^{\mathrm{T},\alpha}$ is a pure dilation, the solute redistribution in α is driven by the non-uniformity of a hydrostatic component of the matrix stress field alone. In this case and when $e^{\mathrm{T},\beta}$ is a pure dilation no solute redistribution will take place and the matrix composition will remain uniform. Hence, should an orthorhombic $e^{\mathrm{T},\beta}$ of the M_2C phase be dominated by its volumetric part, the solute redistribution is expected to be minor. This approximation will be made in the present paper.

Under the assumptions made above, conditions for the chemical and mechanical equilibrium can be defined by the equality of diffusion potentials in the two phases and can then be written as:

$$\begin{aligned} & M^{\alpha}_{\mathrm{FeCr}}(y^{\alpha}_{\mathrm{Cr}}, y^{\alpha}_{\mathrm{Mo}}, y^{\alpha}_{\mathrm{Ni}}, y^{\alpha}_{\mathrm{Co}}, y^{\alpha}_{\mathrm{C}}) \\ = \; & M^{\beta}_{\mathrm{FeCr}}(y^{\beta}_{\mathrm{Cr}}, y^{\beta}_{\mathrm{Mo}}, y^{\beta}_{\mathrm{C}}, \sigma^{\beta}_{\mathrm{ij}}) \end{aligned} \tag{1a}$$

$$\begin{aligned} & M^{\alpha}_{\mathrm{FeMo}}(y^{\alpha}_{\mathrm{Cr}}, y^{\alpha}_{\mathrm{Mo}}, y^{\alpha}_{\mathrm{Ni}}, y^{\alpha}_{\mathrm{Co}}, y^{\alpha}_{\mathrm{C}}) \\ = \; & M^{\beta}_{\mathrm{FeMo}}(y^{\beta}_{\mathrm{Cr}}, y^{\beta}_{\mathrm{Mo}}, y^{\beta}_{\mathrm{C}}, \sigma^{\beta}_{\mathrm{ij}}) \end{aligned} \tag{1b}$$

$$\begin{aligned} & M^{\alpha}_{\mathrm{CVa}}(y^{\alpha}_{\mathrm{Cr}}, y^{\alpha}_{\mathrm{Mo}}, y^{\alpha}_{\mathrm{Ni}}, y^{\alpha}_{\mathrm{Co}}, y^{\alpha}_{\mathrm{C}}) \\ = \; & M^{\beta}_{\mathrm{CVa}}(y^{\beta}_{\mathrm{Cr}}, y^{\beta}_{\mathrm{Mo}}, y^{\beta}_{\mathrm{C}}, \sigma^{\beta}_{\mathrm{ij}} \end{aligned} \tag{1c}$$

where M_{FeCr} is the Fe–Cr diffusion potential in the specified phase, etc. y^{α} and y^{β} are respectively α- and β-phase compositions expressed as site fractions of metal elements Cr, Mo, Ni, and Co on the first sublattice and site fractions of the nonmetal element C on the second sublattice. It has been assumed that Ni and Co do not partition to M_2C, in accordance with recent FIM/atom probe results [9, 10]. y^{α} compositions in Equation 1 pertain to the ferrite matrix phase far from the β-precipitate, where the elastic stresses have fallen to zero (the reference state). $\sigma^{\beta}_{\mathrm{ij}}$ is the uniform stress field in the β phase.

The diffusion potential in a phase with two sublattices at a constant temperature can be written as [8]:

$$\begin{aligned} & M_{\mathrm{IJ}}(y_1, y_{\mathrm{J}}, \ldots, y_{\mathrm{i}}, y_{\mathrm{j}}, \ldots, \sigma_{rr}) \\ = \; & \mu_{\mathrm{I}} - \mu_{\mathrm{J}} - V^{0}_{\mathrm{ref}} \left.\frac{\partial e^{\mathrm{T}}_{rr}}{\partial y_{\mathrm{J}}}\right|_{y_{\mathrm{K}} \neq y_{\mathrm{I}},\, y_{\mathrm{J}} : y_{\mathrm{i}}} \sigma_{rr} \end{aligned} \tag{2}$$

where μ_{I} is a chemical potential of I, etc., $y_{\mathrm{I}}, y_{\mathrm{J}}, \ldots$ and $y_{\mathrm{i}}, y_{\mathrm{j}}, \ldots$ refer to species I, J, ... residing on the first (metallic) sublattice and to species i, j, ... residing on the second (carbon) sublattice, respectively, V^{0}_{ref} is a molar volume of the reference state, e^{T}_{rr}, $rr = 11$, 22 and 33, the principal strains of the stress-free transformation strain.

For α in the stress-free reference state, $e^{\mathrm{T},\alpha}_{rr} = 0$, Equation 2 yields:

$$M^{\alpha}_{\mathrm{FeCr}}(y^{\alpha}_{\mathrm{Cr}}, y^{\alpha}_{\mathrm{Mo}}, y^{\alpha}_{\mathrm{Ni}}, y^{\alpha}_{\mathrm{Co}}, y^{\alpha}_{\mathrm{C}}) = \mu^{2}_{\mathrm{Fe}} - \mu^{\alpha}_{\mathrm{Cr}} \tag{3a}$$

$$M^{\alpha}_{\mathrm{FeMo}}(y^{\alpha}_{\mathrm{Cr}}; y^{\alpha}_{\mathrm{Mo}}, y^{\alpha}_{\mathrm{Ni}}, y^{\alpha}_{\mathrm{Co}}, y^{\alpha}_{\mathrm{C}}) = \mu^{\alpha}_{\mathrm{Fe}} - \mu^{\alpha}_{\mathrm{Mo}} \tag{3b}$$

$$M^{\alpha}_{\mathrm{CVa}}(y^{\alpha}_{\mathrm{Cr}}, y^{\alpha}_{\mathrm{Mo}}, y^{\alpha}_{\mathrm{Ni}}, y^{\alpha}_{\mathrm{Co}}, y^{\alpha}_{\mathrm{C}}) = \mu^{\alpha}_{\mathrm{C}} \tag{3c}$$

Diffusion potentials in the reference state thus depend only on the corresponding α-composition.

According to the generalized Hooke's law the uniform stress field inside β is given as:

$$\begin{aligned} \sigma^{\beta}_{\mathrm{rs}} = \; & \frac{E^{\beta}}{(1 - \nu)} \varepsilon^{\beta}_{\mathrm{rs}} \\ & + \frac{\nu E^{\beta}}{(1 + \nu)(1 - 2\nu)} \left[\varepsilon^{\beta}_{11} + \varepsilon^{\beta}_{22} + \varepsilon^{\beta}_{33} \right] \delta_{\mathrm{rs}} \end{aligned} \tag{4}$$

where E and ν are the Young's modulus and the Poisson's ratio, respectively, δ_{rs} the Kronecker delta and ε^{β} the total strain in β.

Recent FIM [9] and TEM [6] indicate that coherently precipitating M_2C carbides in AF1410 are prolate spheroidal with an aspect ratio ranging from 1 at nucleation to 3 at completion of precipitation. We here approximate β particles as spherical. For a β particle of the spherical morphology ε^{β} is related to the corresponding stress-free transformation strain, $e^{\mathrm{T},\beta}$, by the following relation:

$$\varepsilon^{\beta}_{\mathrm{rr}} = (S_{1111} - 1)\, e^{\mathrm{T},\beta}_{rr} + S_{1122}\,(e^{\mathrm{T},\beta}_{\mathrm{ss}} + e^{\mathrm{T},\beta}_{\mathrm{tt}}) \tag{5}$$

where S_{1111} and S_{1122} are two independent elements of the Eshelby matrix [11] defined as:

$$S_{1111} = \frac{7 - 5\nu}{15(1 - \nu)} \tag{6a}$$

$$S_{1122} = \frac{5\nu - 1}{15(1 - \nu)} \tag{6b}$$

Upon substitution of Equations 6a and 6b into Equation 5 and in turn in Equation 4, and setting $\nu = 0.3$, we obtain:

$$\sigma^{\beta}_{rr} = E^{\beta}\,[2.375 e^{\mathrm{T},\beta}_{rr} + 2.075\,(e^{\mathrm{T},\beta}_{\mathrm{ss}} + e^{\mathrm{T},\beta}_{\mathrm{tt}})] \tag{7}$$

The M_2C carbide phase has a hcp structure with lattice parameters, a^{β} and c^{β}. Octahedral sites in this structure form a simple hexagonal lattice with lattice parameters a^{β} and $0.5c^{\beta}$. The number of octahedral sites is the same as that of metallic sites but only one half to one third of the former are actually occupied by carbon atoms.

The orientation relationship between M_2C carbide precipitates and ferrite matrix, as originally determined by Dyson [12], is shown in Fig. 1. It is seen that

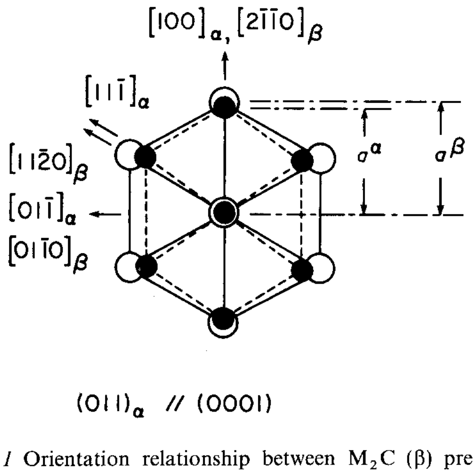

Figure 1 Orientation relationship between M_2C (β) precipitate phase and ferrite (α) matrix phase. Metallic sites (●) α, (○) β.

$(0\,1\,1)_\alpha \| (0\,0\,0\,1)_\beta$ and that in these planes the best matching is achieved along $[0\,1\,\bar{1}]_\alpha \| [0\,1\,\bar{1}\,0]_\beta$. The ferrite/$M_2C$ lattice correspondence is commonly expressed not with respect to the hexagonal but rather with respect to an orthorhombic lattice of the M_2C phase. The relationship between the two M_2C lattices and their parameters can be expressed as:

$$\begin{aligned} [1\,0\,0]^{\mathrm{orth}}_\beta &= [2\,\bar{1}\,\bar{1}\,0]^{\mathrm{hex}}_\beta \\ [0\,1\,0]^{\mathrm{orth}}_\beta &= [0\,1\,\bar{1}\,0]^{\mathrm{hex}}_\beta \\ [0\,0\,1]^{\mathrm{orth}}_\beta &= [0\,0\,0\,1]^{\mathrm{hex}}_\beta \end{aligned}$$

and

$$a^0 = a^\beta, \mathrm{b}^0 = 3^{1/2}\,a^\beta, \text{and } c^0 = c^\beta.$$

Ferrite/M_2C lattice correspondence is then defined as:

$$\begin{aligned} [1\,0\,0]^{\mathrm{orth}}_\beta &\leftrightarrow [1\,0\,0]^{\mathrm{bcc}}_\alpha \\ [0\,1\,0]^{\mathrm{orth}}_\beta &\leftrightarrow [0\,1\,\bar{1}]^{\mathrm{bcc}}_\alpha \\ [0\,0\,1]^{\mathrm{orth}}_\beta &\leftrightarrow [0\,1\,1]^{\mathrm{bcc}}_\alpha \end{aligned}$$

The principal strains of the orthorhombic distortion relating the two structures, α and β, are then:

$$\begin{aligned} e^{\mathrm{T},\beta}_{11} &= a^0/a^\alpha - 1 = a^\beta/a^\alpha - 1 \\ e^{\mathrm{T},\beta}_{22} &= 2^{-1/2} b^0/a^\alpha - 1 = (1.5)^{1/2} a^\beta/a^\alpha - 1 \\ e^{\mathrm{T},\beta}_{33} &= 2^{-1/2}\, c^0/a^\alpha - 1 = (2)^{-1/2}\, c^\beta/a^\alpha - 1 \quad (8) \end{aligned}$$

with a^α being generally a function of the ferrite composition and a^β, c^β, a^0, b^0, and c^0 being functions of the composition of M_2C. However, since the elastic coherency is not expected to alter appreciably the composition of α in the stress-free reference state, in the following the α-lattice parameter will be considered constant and equal to its value in a well-overaged state, 0.287 nm [6].

Lattice parameters of several M_2C carbides have been listed in Table I. Under the assumption that the effect of carbon deficiency on the M_2C lattice parameters is independent of the composition of the metallic sublattice, data in Table I have been used to fit the principal strains with a function [13]:

$$e^{\mathrm{T},\beta}_{rr} = \sum_{\mathrm{I=Cr,Mo,Fe}} \sum_{\mathrm{i=C,Va}} A^{rr}_{\mathrm{I:i}}\, y^\beta_{\mathrm{I}}\, y^\beta_{\mathrm{i}} \qquad (9)$$

where Va are vacancies residing on the nonmetal sublattice. The values of the coefficients $A^{rr}_{\mathrm{I:i}}$ are given in Table II.

For $e^{\mathrm{T}.\beta}$ given by Equation 9 σ^β_{rr} becomes:

$$\sigma^\beta_{rr} = E^\beta \sum_{\mathrm{I=Cr,Mo,Fe}} \sum_{\mathrm{i=C,Va}} B^{rr}_{\mathrm{I:i}}\, y^\beta_{\mathrm{I}}\, y^\beta_{\mathrm{i}} \qquad (10a)$$

where

$$B^{rr}_{\mathrm{I:i}} = 2.375\mathrm{A}^{rr}_{\mathrm{I:i}} + 2.075(A^{\mathrm{ss}}_{\mathrm{I:i}} + A^{\mathrm{tt}}_{\mathrm{I:i}}) \qquad (10b)$$

TABLE I Hexagonal lattice parameters of various M_2C carbides [6]

Carbide	a^β (nm)	c^β (nm)
Fe_2C	0.2752	0.4355
Cr_2C	0.2790	0.4460
Mo_2C	0.3000	0.4720
$Mo_2C_{0.9}$	0.2997	0.4727
$(Mo_{0.36}Cr_{0.64})_2C$	0.3000	0.4735

TABLE II Values of $A^{rr}_{\mathrm{I:i}}$ coefficients in Equation 9 [13]

$A^{rr}_{\mathrm{I:i}}$		rr		
I	i	11	22	33
Cr	C	− 0.1313	+ 0.1865	+ 0.0950
	Va	− 0.0833	+ 0.1227	+ 0.0803
Fe	C	− 0.0444	+ 0.1703	+ 0.0688
	Va	− 0.0965	+ 0.1065	+ 0.0540
Mo	C	+ 0.0580	+ 0.2809	+ 0.1621
	Va	− 0.0630	+ 0.2745	+ 0.1473

Furthermore, from Equation 9 the following relations can be derived:

$$\left.\frac{\partial e^{\mathrm{T},\beta}_{rr}}{\partial y^\beta_{\mathrm{I}}}\right|_{y_{\mathrm{J}} \neq y^\beta_{\mathrm{I}}, y^\beta_{\mathrm{Fe}}; y^\beta_{\mathrm{C}}} = A^{rr}_{\mathrm{I:Va}} + C^{rr}_{\mathrm{I}}\, y^\beta_{\mathrm{C}} \qquad (11a)$$

where (I, J = Cr, Mo)

$$\left.\frac{\partial e^{\mathrm{T},\beta}_{\mathrm{rr}}}{\partial y^\beta_{\mathrm{i}}}\right|_{y_{\mathrm{I}}, y_{\mathrm{J}}} = -A^{rr}_{\mathrm{Fe:Va}} + \sum_{\mathrm{I=Cr,Mo}} C^{rr}_{\mathrm{I}}\, y^\beta_{\mathrm{I}} \qquad (11b)$$

where

$$C^{rr}_{\mathrm{I}} = [A^{rr}_{\mathrm{I:C}} - A^{rr}_{\mathrm{I:Va}} - A^{rr}_{\mathrm{Fe:C}} - A^{rr}_{\mathrm{Fe:Va}}] \qquad (11c)$$

Upon substitution of Equations 10a, 11a, and 11b into Equation 2 we obtain

$$\begin{aligned} M^\beta_{\mathrm{FeCr}} &= \mu^\beta_{\mathrm{Fe}} - \mu^\beta_{\mathrm{Cr}} - V^0_{\mathrm{ref}} E^\beta \\ &\quad \times \sum_{rr=11}^{33} (A^{rr}_{\mathrm{Cr:Va}} + B^{rr}_{\mathrm{Cr}}\, y^\beta_{\mathrm{C}}) \\ &\quad \times \left[\sum_{\mathrm{I=Cr,Mo,Fe}} \sum_{\mathrm{i=C,Va}} C^{rr}_{\mathrm{I:i}}\, y^\beta_{\mathrm{I}} y^\beta_{\mathrm{i}}\right] \qquad (12a) \\ M^\beta_{\mathrm{FeMo}} &= \mu^\beta_{\mathrm{Fe}} - \mu^\beta_{\mathrm{Mo}} - V^0_{\mathrm{ref}}\, E^\beta \\ &\quad \times \sum_{rr=11}^{33} (A^{rr}_{\mathrm{Mo:Va}} + B^{rr}_{\mathrm{Mo}}\, y^\beta_{\mathrm{C}}) \\ &\quad \times \left[\sum_{\mathrm{I=Cr,Mo,Fe}} \sum_{\mathrm{i=C,Va}} C^{rr}_{\mathrm{I:i}}\, y^\beta_{\mathrm{I}} y^\beta_{\mathrm{i}}\right] \qquad (12b) \\ M^\beta_{\mathrm{CVa}} &= \mu^\beta_{\mathrm{C}} - V^0_{\mathrm{ref}} E^\beta \\ &\quad \times \sum_{rr=11}^{33} \left(-A^{rr}_{\mathrm{Fe:Va}} + \sum_{\mathrm{I=Cr,Mo}} B^{rr}_{\mathrm{I}}\, y^\beta_{\mathrm{I}}\right) \\ &\quad \times \left[\sum_{\mathrm{J=Cr,Mo,Fe}} \sum_{\mathrm{i=C,Va}} C^{rr}_{\mathrm{J:i}}\, y^\beta_{\mathrm{J}}\, y^\beta_{\mathrm{i}}\right] \qquad (12c) \end{aligned}$$

In accordance with the previous assumption regarding the composition independent a^α parameter, the molar volume of ferrite in the reference state, V^0_{ref}, should be set to a fixed value of 1.182×10^{-29} m^3. All other quantities in Equations 12a to 12c are functions of the β-phase composition.

The composition dependence of chemical potentials in multicomponent nonstoichiometric phases with two sublattices, such as ferrite and M_2C-carbide, has been recently analysed by Hillert [14]. The following relations have been obtained:

$$\mu_{\mathrm{I}} = \mu^{\mathrm{id}}_{\mathrm{I}} + \mu^{\mathrm{ex}}_{\mathrm{I}} \quad (\mathrm{I} = \mathrm{Cr, Mo, Fe}) \qquad (13a)$$

where μ_I^{id} is the chemical potential of a metallic species I in an ideal solution, and

$$\begin{aligned} a\mu_I^{ex} = & -{}^0L^I_{C:Va}\,y_C[1 - y_C - y_I + 2y_Iy_C] \\ & -{}^1L^I_{C:Va}\,y_C[(1 - 2y_C) \\ & \times(1 - y_C - y_I + 3y_Iy_C) + y_Iy_C] \\ & -\sum_{J\neq I}{}^0L^J_{C:Va}\,y_J\,y_C(-1 + 2y_C) \\ & -{}^1L^J_{C:Va}\,y_Jy_C[(1 - 2y_C)(3y_C - 1) + y_C] \end{aligned} \tag{13b}$$

Also,

$$\mu_C = \mu_C^{id} + \mu_C^{ex} \tag{14a}$$

and

$$\begin{aligned} c\mu_C^{ex} = & \sum_{I=Cr,Mo,Fe}{}^0L^I_{C:Va}\,y_I(1 - 2y_C) \\ & + {}^1L^I_{C:Va}\,y_I(-1 + 6y_C - 6y_C^2) \end{aligned} \tag{14b}$$

where ${}^0L^I_{C:Va}$ and ${}^1L^I_{C:Va}$ are respectively the regular and subregular chemical interaction parameters in the Redlich-Kister extrapolation formula for the integral molar excess Gibbs free energy [15], and pertain to the interaction between interstitial atoms and vacancies when the metal sublattice is occupied by a species I, a and c are respectively the number of sites on the metal and nonmetal sublattices per one mole of chemical formula ($a = 1/4$, $c = 3/4$ for ferrite and $a = 2/3$ and $c = 1/3$ for M_2C).

Upon substitution of Equations 3a to 3c and 12a to 12c into Equations 1a to 1c we obtain a set of three equations connecting the equilibrium composition of ferrite (y_{Cr}^α, y_{Mo}^α, y_{Ni}^α, y_{Co}^α, y_C^α) and the equilibrium composition of M_2C (y_{Cr}^β, y_{Mo}^β, y_C^β).

The remaining interfacial condition necessary for equilibrium fixes the jump in grand canonical free energy, ω, across the α/β interface [16]. In the limit of linear isotropic elasticity and under assumption that the $\omega^\alpha - \omega^\beta$ jump is dominated by the volumetric part of $e^{T,\beta}$ the interfacial equilibrium requires the following jump in chemical potential of iron across the interface [6]:

$$\mu_{Fe}^\alpha - \mu_{Fe}^\beta = V_{ref}^0\frac{(e^{t,\beta})^2E^\alpha E^\beta(4 - 7\nu)}{9[2E^\alpha(1 - 2\nu) + E^\beta(1 + \nu)]} \tag{15a}$$

where

$$e^{t,\beta} = e_{11}^{T,\beta} + e_{22}^{T,\beta} + e_{33}^{T,\beta} \tag{15b}$$

Relation 15a is strictly valid only when $e^{T,\beta}$ is a pure dilation and hence the matrix stress field is a zero-trace pure shear and as a result the matrix composition is uniform. In the case of an orthorhombic $e^{T,\beta}$, on the other hand, the stress trace and hence solute distribution in the matrix are nonuniform. In addition, since $e^{T,\beta}$ is an invariant line strain ($e_{11}^{T,\beta} < 0$, $e_{22}^{T,\beta}$, $e_{33}^{T,\beta} > 0$) the stress trace takes on both positive and negative values at the α/β interface. We here assume that at those points at the interface, where the trace is zero, and thus an interfacial matrix composition is the same as that in the reference state, the $\mu_{Fe}^\alpha - \mu_{Fe}^\beta$ jump can be approximated by the corresponding quantity for an equivalent pure dilation $e^{T,\beta}$ having the same transformation volume change.

Further relations connecting equilibrium compositions of the two phases can be obtained from the mass balance conditions:

$$\frac{y_{Cr}^0}{y_C^0 + a/c} = f^\alpha\frac{y_{Cr}^\alpha}{y_C^\alpha + a/c} + (1 - f^\alpha)\frac{y_{Cr}^\alpha}{y_C^\beta + a/c} \tag{16}$$

$$\frac{y_{Mo}^0}{y_C^0 + a/c} = f^\alpha\frac{y_{Mo}^\alpha}{y_C^\alpha + a/c} + (1 - f^\alpha)\frac{y_{Mo}^\beta}{y_C^\beta + a/c} \tag{17}$$

$$\frac{y_{Ni}^0}{y_C^0 + a/c} = f^\alpha\frac{y_{Ni}^\alpha}{y_C^\alpha + a/c} \tag{18}$$

$$\frac{y_{Co}^0}{y_C^0 + a/c} = f^\alpha\frac{y_{Co}^\alpha}{y_C^\alpha + a/c} \tag{19}$$

$$\frac{y_C^0}{y_C^0 + a/c} = f^\alpha\frac{y_C^\alpha}{y_C^\alpha + a/c} + (1 - f^\alpha)\frac{y_C^\beta}{y_C^\beta + a/c} \tag{20}$$

where y_{Cr}^0 is the nominal concentration of chromium in the alloy, etc. f^α is the mole fraction of the α-phase.

Equations 1a to 1c, 15a and 16 through 20 define a system of nine nonlinear equations with nine unknowns, y_{Cr}^α, y_{Mo}^α, y_{Ni}^α, y_{Co}^α, y_C^α, f^α, y_{Cr}^β, y_{Mo}^β, y_C^β which can be solved using the Newton–Raphson iteration method.

In the next section we use the model developed above to determine the coherent ferrite/M_2C equilibrium at 783 K in AF1410 and SRG1 steels. To simplify the calculation it is assumed that ferrite and M_2C have the same, composition-independent Young's modulus, 225.5 GPa [12]. Chemical interaction parameters have been taken from a recent assessment of the Fe–Co–Ni–Cr–Mo–C system [17].

3. Results and discussion

Calculated composition of the equilibrium coherent M_2C carbide in the AF1410 steel at the standard secondary hardening temperature of 783 K are shown in Table III. Also shown in Table III are the results of our calculation for the incoherent ferrite/M_2C equilibrium and for the most probable composition of a β nucleus. The THERMOCALC computer program [18], which utilizes the condition for equality of chemical potentials in the two phases has been employed for calculation of the incoherent equilibrium. For the case of the unstable equilibrium that prevails during nucleation from the fully supersaturated matrix, the contribution of capillarity has been treated within the approximation of a composition-independent isotropic interfacial energy by increasing the molar Gibbs free energy of β by a constant. It was shown elsewhere [13, 19] that under such conditions the most probable composition of a coherent nucleus can still be found by maximizing the driving force for nucleation. This calculation has also been carried out using THERMOCALC.

TABLE III Comparison of calculated and measured compositions of the M_2C phase in an AF1410 steel at 783 K

	Condition	M_2C composition
Model predictions	Coherent nucleation	$(Cr_{0.49}Mo_{0.39}Fe_{0.12})_2C_{0.79}$
	Coherent equilibrium	$(Cr_{0.62}Mo_{0.32}Fe_{0.06})_2C_{0.83}$
	Incoherent equilibrium	$(Cr_{0.64}Mo_{0.36}Fe_{0.00})_2C_{1.0}$
AP/FIM	783 K, 5 h temper	$(Cr_{0.58\pm0.03}Mo_{0.36\pm0.03}Fe_{0.06\pm0.03})_2C_{0.81\pm0.03}$
Measured [9]	783 K, 8 h temper	$(Cr_{0.64\pm0.01}Mo_{0.30\pm0.01}Fe_{0.06\pm0.01})_2C_{0.89\pm0.01}$

TABLE IV Comparison of calculated and measured compositions of the M_2C phase in an SRG1 steel at 783 K

	Condition	M_2C composition
Model predictions	Coherent nucleation	$(Mo_{0.93}Fe_{0.07})_2C_{0.75}$
	Coherent equilibrium	$(Mo_{0.94}Fe_{0.06})_2C_{0.84}$
	Incoherent equilibrium	$(Mo_{0.99}Fe_{0.01})_2C_{1.0}$
AP/FIM [9]	783 K, 8 h temper	$(Mo_{0.96\pm0.02}Fe_{0.04\pm0.01})_2C_{0.88\pm0.02}$

Compared to the incoherent equilibrium composition, the predicted coherent equilibrium composition shows a significant carbon deficiency, an enhanced iron solubility and a slight reduction in chromium, in line with the influence of these constituents in reducing the principal transformation strains of Equation 8. For example, the smallest principal transformation strain, $\varepsilon_{11}^{T;\beta}$, has been lowered from its values of $+0.0580$, -0.0444 and -0.0313 in Mo_2C, Cr_2C and Fe_2C, respectively, to -0.0094 in the $(Cr_{0.62}Mo_{0.32}Fe_{0.06})_2C_{0.83}$ coherent carbide. Thus along $[1\,0\,0]_\alpha \parallel [2\,\bar{1}\,\bar{1}\,0]_\beta$ the principal transformation strain is near zero and since the other principal strains are both positive, $\varepsilon_{22}^{T;\beta} = +0.2205$ and $\varepsilon_{33}^{T;\beta} = +0.1296$, the stress-free transformation strain for β is close to an invariant line strain. This leads to a substantial reduction of the elastic strain energy in the two-phase ferrite/M_2C coherent system. Further reduction in the strain energy is obtained through β particles adopting a prolate spheroidal shape with the major axis in the direction of minimum distortion, $[1\,0\,0]_\alpha \parallel [2\,\bar{1}\,\bar{1}\,0]_\beta$, [6].

The deviations from the incoherent equilibrium composition are further enhanced for the predicted coherent nucleus composition. The sequence of compositions corresponding to coherent nucleation → coherent equilibrium → incoherent equilibrium outlines the carbide composition trajectory for the complete M_2C precipitation process. The nature of the carbide composition trajectory during precipitation is thus to approach the incoherent composition following a direction of increasing carbon, decreasing iron, and increasing chromium.

Also shown in Table III for comparison purposes are recent results of an AP/FIM microanalysis study [9] giving measured compositions of the M_2C carbides in AF1410 for tempering treatment of 5 and 8 h at 783 K. Composition uncertainties are expressed as ± 2 standard deviations. As mentioned earlier measured carbide lattice parameter shifts relative to the well-overaged incoherent state suggest the M_2C phase is coherent at these tempering times, and the nearly complete dissolution of cementite suggests that M_2C precipitation is complete. Hence the 5–8 h tempered state should be close to coherent equilibrium. That the observed compositions bracket the predicted coherent equilibrium composition shows excellent agreement between theory and experiment, confirming the predicted composition departures from the incoherent equilibrium state. The composition differences between the 5 and 8 h treatments also imply a composition trajectory in the direction predicted.

Table IV lists results of our calculation and AP/FIM microanalysis [9] of the M_2C coherent nucleation and the coherent and the incoherent ferrite/M_2C equilibria at the standard secondary hardening temperature of 783 K in the SRG1 steel. As in the case of AF1410 the coherent carbide composition indicates a significant carbon deficiency and a measurable iron solubility and the composition trajectory for the complete M_2C precipitation process is such to approach the incoherent composition following a direction of increasing carbon and decreasing iron.

4. Conclusions

Composition of coherent M_2C carbides in high Co–Ni martensitic steels can be calculated using conditions for mechanical, chemical and interfacial equilibrium in a two-phase coherent system with a small volume fraction of the precipitate phase, where the stress-free transformation strain of the matrix is a pure dilation and the transformation strain of the precipitate is a general composition-dependent orthorhombic strain. Calculated compositions are in a very good agreement with available AP/FIM results. Deviations of coherent M_2C compositions from the corresponding incoherent compositions are such to reduce the principal strains of the M_2C stress-free transformation strain and hence the elastic energy.

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